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Vol. 29. No. 235. July 1943.

Editorial Note.—*With the greatly broadened scope of membership and the change in character of the Institute of Petroleum, the Council has felt the time ripe to undertake the preparation of a work under the title of "Modern Petroleum Technology" which shall present to its readers a composite picture of the present state of petroleum technology.*

The aim of this series of articles is that they will be primarily of general interest to all classes of members of the Institute and, although not popular in the generally accepted sense of the word, that they shall convey the knowledge of the specialist in an intelligent and educative manner to his less specialized confreres in the industry.

While the proposal is to publish the series in the form of a manual of petroleum technology, it is hoped that the articles will first be published, as received, in the Journal.

CHEMISTRY AND THE PETROLEUM INDUSTRY.*

By A. E. Dunstan, D.Sc. (Lond.), F.I.C.

So important has become the petroleum industry in our own generation that it is impossible to put forward any but the barest summary of the impact on it of the chemist—and yet in all its phases it has been a lively centre of chemical activity, and promises in the near future to become more than ever a most important branch of applied chemistry.

It is of some interest to look back through barely two spans of human life to the development of the industrial application of mineral oil. To those who regard the origins of things as of some importance, attention might well be directed to the Cantor Lectures of the late Sir Boverton Redwood in 1886. At that time by distillation was merely comprehended the boiling of oil and the condensation of its vapours—little or no attempt was made at effecting close fractionation. Chemical refining of products was a more or less brutal attack by means of strong sulphuric acid. There were scant references to a new line of approach to modern developments, that is to say, the "cracking" of heavy hydrocarbons as practised at Nobel's Refinery at Baku, whereby substantial yields of aromatic hydrocarbons were obtained. Very significant was the statement that "by far the most important of the uses to which the products of petroleum are as yet applied is that of illumination." At the close of his lectures Redwood suggested "that the degree of mental culture of a nation may be measured by the quantity of mineral oil consumed"—a prophecy which reads somewhat grimly during the course of two subsequent World Wars. It is, however, patently obvious that our everyday life in peace depends for its very existence, its amenities, and its luxuries on petroleum, and in war-time, with even more emphasis, the very narrow margin between survival and defeat depends on supplies of aviation spirit, gasoline, liquid fuel, and lubricants. Just before 1939 over thirty million motor vehicles transported man, his food, and his raw materials. It is not necessary here to dwell on the urgent need of mechanized warfare, of military aviation, and of the imperative demands of navies.

The production of petroleum in the world, in round figures, is of the order of 250 million tons a year. Considering the quantity of petroleum produced ever since the beginning of the industry (about 80 years), the whole of that production, if put into one tank, would amount to

* This article is based on a lecture given in 1942 to the Royal Institute of Chemistry.

less than a cubic mile. It will be interesting to take one or two comparative figures. The amount of water which goes into one of the largest of the Thames reservoirs is 50 million gallons a day, or 80 million tons a year. In other words, even by comparison with the water required for one city, the world's production of petroleum is relatively small.

TABLE I.

Production.

World production of petroleum, 1886	3,000,000 tons
World production of petroleum, 1927	170,000,000 tons
World production of petroleum, 1938	268,000,000 tons
Annual production of natural gas (approx.)	3,000,000,000,000 cub. ft.
Annual production of cracked gas	300,000,000,000 cub. ft.
Coal gas made for the United Kingdom in 1937, of which one-tenth was produced by the Gas Light and Coke Co.	550,000,000,000 cub. ft.

TABLE II.

Percentage Production of Petroleum by Countries, 1940.

United States	63
Other countries (Russia, Mexico, South America, Iran, Iraq)	34
British Empire	3

Further figures are given by Egloff for the year 1941 :—

TABLE III.

	World crude oil production.	
	1000 barrels.	Per cent.
United States	1,400,000	62·5
Mexico	41,200	1·8
Canada	10,000	0·4
Central and South America	300,000	13·5
Europe	295,000	13·1
Asia	113,000	5·0
Oceania	71,600	3·2
Other countries	8,000	0·4
World total (approx.)	2,250,000	—

TABLE IV.

Production of Oil Shale, 1938.

	Tons.
United Kingdom	1,500,000
Estonia	1,450,000
U.S.S.R. (estimated, 1936)	700,000
France	130,000

Production.

Modern search for oil lies mainly in the province of the geologist and his colleague, the geophysicist, but the chemist also plays his part, and the

latest petroleum science—that of geochemistry—is becoming important, as witness the careful analysis of superjacent soil, and of underlying formations for adsorbed gaseous hydrocarbons, symptomatic of underground seepages.

It would be out of place here even to outline the intricacies of the drilling technique. But it may be briefly indicated that metallurgical science is called into play to determine the appropriate steels to be used, capable of withstanding immense stresses and able to cope with outstanding problems of corrosion, and that the colloid chemist has to decide on appropriate mixtures of clays and weighting material, to coat the hole effectively to withstand sudden gas pressures, to hold in suspension drilled-out material, and to possess rather specialized physical properties of viscosity and thixotropy. And, furthermore, it should be noted that the chemist in the oil-fields has a multiplicity of functions apart from those related to the actual sinking of the well. He is a very essential colleague of his geological confrères. Samples of oil and gas and bitumen go to him—he must be able to determine the physical constants of the fluid in the oil horizon, gas–oil ratios, for example, viscosities under very high pressures, solubilities, retrograde condensation phenomena, plant efficiency in absorption or compression units. More and more he is concerned in the design and operation of the multifarious types of fields plant.

Gas.

When the oil formation is struck, there is usually encountered considerable gas pressure, and a mixture of oil and gas rushes out. This solution may be regarded as crude mineral oil. In effect it is a mixture of solids, liquids, and gases, not only in true physical solution, but also co-existing in the colloidal state. The gas component is in the main methane, but also present are ethane, propane, the butanes, and pentanes, with relatively small amounts of hydrogen sulphide, water vapour, carbon dioxide, nitrogen, and, in some cases, helium. Some analyses follow :—

TABLE V.

	CH_4.	C_2H_6.	C_3H_8.	C_4H_{10}.	N_2.	CO_2.	H_2S.	He.
A typical "dry" gas (sp. gr. 0·65) . . .	84·7	9·4	3·0	1·3	1·6	trace	—	—
A "wet" gas (sp. gr. 1·38) . . .	18·0	—	—	78·7	3·3	—	—	—
A sulphurous gas . .	40	21	18	9	—	—	12	—
A helium-containing gas.	15	—	—	—	83	—	—	2

It should be noted that a "dry" gas contains little that is liquefiable under ordinary conditions of temperature and pressure, whilst a "wet" gas may contain considerable amounts of hydrocarbons available for incorporation into motor fuel. Natural gas contains many components which are of value, and every effort is made to conserve them. In the first place, the fluid mixture passes straightaway from the well into a high-pressure separator. This is, in effect, a long cylinder in which separation takes place at, for example, 2000 lb./sq. in. At that pressure

the free gas will be mainly methane; if, then, the pressure is released in a series of vessels, stage by stage, for instance, to 600 lb., and then to 65 or 50 lb., there is a rough separation in each unit of the various gases which are incidental to the production of the crude oil.

Unfortunately, the largest proportion of the gas is methane, and this is without doubt a recalcitrant hydrocarbon. The higher homologues, however, are more amenable to treatment.

It will be noticed from the analyses in Table V that a rare component of certain natural gases (*e.g.*, from certain Texas fields) is helium. This gas is now separated by means of intensive refrigeration and used as the lifting agent in lighter-than-air dirigibles.

Brief reference should here be made to the utilization of the great bulk of the C_3 and C_4 fractions, both of natural and cracker (*q.v.*) gas. This material is readily liquefied under moderate pressure, and constitutes "bottled gas"—sold under various names, *e.g.*, calorgas, propagas, and the like. In 1941, the United States consumed 460,000,000 gallons of this liquid, and it is of some import to realize that the sales were quadrupled in five years.

The gas coming away from the crude will carry with it a certain amount of hydrocarbon material of higher boiling-point, and, to conserve this material, the gases are stripped in a counter-current system against a solvent heavy oil, just as in the familiar benzol recovery plant in the coal-

TABLE VI.

Production of Liquefied Petroleum Gases in the U.S.A.

Year.	Gallons.
1920 . . .	200,000
1930 . . .	18,000,000
1940 . . .	300,000,000
1941 . . .	460,000,000

TABLE VII.

The Main Constituents of Natural Gas.

	M. p., ° C.	B. p., ° C.
Methane	−182	−161
Ethane	−172	− 89
Propane	−187	− 42
n-Butane	−135	− 0·6
*iso*Butane	−145	− 10
n-Pentane	—	+ 37

tar industry. Solid adsorbents may replace the stripping oil, or, more simply, a compression system may be employed. In this way is made available a very light spirit—natural gasoline—useful for improving the volatility of straight-run petrol and, furthermore, of value as an anti-knock component of motor spirit. (See Figs. 1, 2, 3, 4.)

After the crude oil is thus separated, it still contains some gas in solution, and this is taken out by a converse or stabilizing process in which the crude is heated and the so-called permanent gases in solution, up to

butane, are removed. In turn, they themselves, with various refinery and cracked gases, are stripped of anything they have taken with them in the way of liquefiable content.

The Engine and its Fuel.

Mention should here be made of the behaviour of the various light fractions of mineral oil in the internal-combustion engine. Until com-

TABLE VIII.

Engine Tests of the Commoner Lower Hydrocarbons, etc.

	Octane number. C.F.R.* rating, A.S.T.M.
ISO-OCTANE	100
CH_4	110
C_2H_6	104
C_3H_8	100
n-C_4H_{10}	92
iso-C_4H_{10}	99
n-C_5H_{12}	61
iso-C_5H_{12} { 2-Methylbutane	89
iso-C_5H_{12} { Dimethylpropane	83
n-C_6H_{14}	25
n-C_7H_{16}	80
2 : 3-Dimethylbutane	95
2-Methylpentane	70
3-Methylpentane	80
n-C_7H_{16}	0
2 : 2-Dimethylpentane	93
n-C_8H_{18}	−17
iso-C_8H_{18}	100
i.e. 2 : 2 : 4- and 2 : 2 : 3-Trimethylpentanes	102
n-C_9H_{20}	−45
C_2H_4	81
C_3H_6	85
n-C_4H_8	83
n-C_5H_{10}	80
n-C_6H_{12}	78
Ethyl*cyclo*butane	68
*cyclo*Pentane	83
*cyclo*Hexane	86
Methyl*cyclo*hexane	71
Neohexane	96
C_3H_4	80
C_4H_6	108
C_7H_8	104
For comparison there may be given corresponding data for alcohols, ethers, and ketones :—	
CH_3OH	98
C_2H_5OH	99
n-C_3H_7OH	90
n-C_4H_9OH	87
iso-C_3H_7OH	104
iso-C_4H_9OH	88
$CH_3{\cdot}CO{\cdot}CH_3$	100
$C_2H_5{\cdot}CO{\cdot}CH_3$	99
$CH_3{\cdot}O{\cdot}C_2H_7$	73
$C_2H_7{-}O{-}C_2H_7$	—
N-HEPTANE	0

* See Egloff and Arsdell, *J. Inst. Petrol.*, 1941, **27**, 211 *et seq.*

paratively recently any mixture of straight-run hydrocarbons derived from natural gas and from crude oil would function satisfactorily in the engine, simply because the engine was so designed as to possess a low compression ratio. As the demand for extra efficiency grew more clamant and higher compression ratios were demanded, it was found that such fuels as were indicated above—*i.e.*, straight-run distillates—failed. It will be seen in the sequel that "cracking" helped to ease the situation; but it is rather important to realize that the entity of straight spirit contains components—good and bad—from the point of view of engine performance. Bad are the normal paraffins above C_5—*i.e.*, *n*-hexane and its homologues. Good are the *iso*-paraffins—*iso*pentane and its homologues—and it is of interest to note that in the scale of behaviour first set forth by Graham Edgar, *n*-heptane was the worst and *iso*-octane the best, and in fact the octane number of a fuel takes its place on the scale

n-heptane = 0.
iso-octane = 100.

It is clear, therefore, that careful fractionation, under the highly specialized technique now obtaining, will suffice to split straight hydrocarbon spirit into material of superlative or negligible performance in the engine.

It is appropriate here to consider the entirely revolutionary impact of lead tetraethyl on the octane rating of motor spirit—especially straight run from the crude and by synthesis from the lower hydrocarbon gases. It would be out of place to discuss the manufacture of this material $Pb(Et)_4$. It, however, is made in colossal quantities, and used in very small concentrations (*e.g.*, 4 c.c. per gallon of spirit).

Annually in recent years 66,000,000 lb. of lead tetraethyl were produced (in effect, enough to raise 20,000,000,000 gallons of spirit 7 points in octane rating).

Reverting again to the degassed and stabilized crude, this material now passes to the refinery proper, wherein the separation into further commercial products is effected.

Distillation.

Fig. 5 shows a modern distillation unit, and it will be noted that there are six main components—the pipe-heaters, the primary flash-tower, the main fractionating column, the vacuum column, the pre-heaters, and condensers. In such a unit the crude oil can be run at *circa* atmospheric pressure to remove gasoline, kerosines, and gas oils, and under a good vacuum to yield lubricating oils and the waxes, together with a final pitch residue.

Progressing from the earlier days, when distillation merely consisted in evaporation and condensation, when sharp fractionation was unknown, and when re-distillation sufficed to produce the simple cuts of gasoline and kerosine, the industry has striven to attain perfection of plant operation and control, which can only be achieved by the application of accurate and scientific procedure. The battery of boilers, so arranged that a gravity flow could be maintained from one to the next and a gradually increasing temperature could be maintained from still to still, with the crudest means of separation, gave place to a series of stills equipped with

elementary columns, and finally to the pipe-still, first developed actually in the cracking plants of a generation ago. (Incidentally, the coal-tar industry was a pioneer here.) The pipe-still possessed accurate control of temperature, heat, input pressure, and velocity of flow. Automatic controls were fitted to control rates of flow, temperatures, and levels.

Whilst in the earlier developments of distillation little more than a primary "topping"—*i.e.*, the removal of the lighter components—gasoline and kerosine—was aimed at, in recent years the complete splitting up of the crude into the whole range of merchantable commodities has been achieved, and in effect this is carried out in three successive stages: firstly, a flash evaporation, using waste heat from highly heated residues, which brings about the removal of the lightest fractions. Secondly, the residue from this stage is further heated in a pipe-still and discharged into the main column, provided with a multiplicity of "decks" or bubble-cap plates in which a rather astonishingly complete separation occurs: Overhead is gasoline—at various decks different products can be segregated, and eventually at the bottom of the tower emerges a residue that may represent, for example, 40 per cent. or 50 per cent. of the crude. Auxiliary heating in the form of live steam may be introduced into the tower. Broadly, the result is that the "white oils" are removed in this column—ranges of gasolines, white spirits, and light solvents, ranges of burning oils up to lighthouse and signal oils, ranges of gas oils—all cut according to desired specifications. The residue is again heated in a further pipe-still, and now passes into a column under reasonably high vacuum. Here takes place the final separation into heavy gas oils, lubricating-oil distillates (often containing solid paraffin waxes), and a final residue of pitch.

It should be pointed out as well that distillation may be employed even in the separation of low-boiling material usually regarded as gaseous—that, for example, *iso*butane may be separated quantitatively from a mixture of the two isomeric butanes.

It should be emphasized here that a peculiar degree of separation may be effected by "superfractionation"; as an example, intensive reflux and a multiplicity of "decks" in the column will achieve the isolation of *iso*-pentane from its congeners.

Cracking.

The cracking operation must now be considered. Up to the beginning of the first world war, all petrol was straight-run from the crude, and the average crude yielded about 20 per cent. of motor gasoline. The increasing demand for motor spirit for aviation, road transport, etc., became so great that it was impossible to meet that need with the amount of crude oil available, the methods then in use, and the impracticability of making more heavy residue than could be commercially used. Therefore, the problem of simplifying the heavy oils by breaking them down to lighter fractions became very urgent, and so the cracking procedure, as we know it to-day, came into existence. In effect, cracking is merely the thermal decomposition of the heavier hydrocarbon molecules into less complicated ones, but it must not be imagined for a moment that from 100 gallons of cracking stock there will be produced 100 gallons of petrol. By no means;

something like 60 gallons of petrol is possible by ordinary thermal cracking. The residue will be much heavier oil, together with gas and coke.

Fig. 6 gives an idea of the immensity of the cracking operation. Here is shown one of a series of plants in which 5 or 6 million gallons a day of heavy oil are processed. Apart from the question of quantity, however, there is the question of quality. Since the last war, the whole aspect of quality of petrol has changed. Compression ratios of internal-combustion engines have gone up, and the yield of power per gallon of petrol consumed has also increased. A gallon of gasoline to-day will do twice as much work as a gallon did 20 years ago. With the modern small, high-compression, high-speed internal-combustion engine, there is a vastly increased efficiency in the utilization of motor spirit. It is a fact that nowadays there is not very much straight-run petrol used. This is a sad commentary on Nature's raw material; in point of fact, Nature is not a particularly good manufacturer. Most of what Nature makes can be improved upon to a very considerable extent. So that if Nature's inherent petrol were used to-day, the motoring world would have to go back 20 years, to the time of the T model Ford, with its compression ratio of 3 to 1. The fact that in a modern engine a compression ratio of 7 or 8 to 1 can be used is just an example of how the oil industry has met the challenge of the automobile engineer. Furthermore, far higher compression ratios are likely to confront us to-morrow.

Actually, up to 30 per cent. increase in power for take-off or climbing has been made possible by replacing 87 octane spirit by 100 octane rating.

Not only is heavy oil cracked into lighter, but the straight-run petrol or light distillate itself is cracked or "reformed" to improve its property of withstanding detonation in the engine.

In effect cracking and reforming are operations necessary for the upgrading of fuel for the internal-combustion engine. But, although the products are superior as anti-knock materials, there are serious problems that follow in train. Firstly, there are produced hydrocarbons of lower stability, with greater capacity for oxidation and proneness to gum formation. Such bodies could be removed by intensive acid treatment—with resultant loss of valuable fuel. And so has been developed the practice of anti-oxidant or inhibitor addition, whereby the chain reactions that lead ultimately to unpleasant end-products are checked. Such materials as the cresols, the amino-phenols, and aromatic dihydroxy derivatives substantially reduce these tendencies.

Perhaps of even greater importance to-day is the concomitant production of unsaturated hydrocarbon gases as a result of this thermal treatment—for example, ethylene, propylene, the butylenes, and amylenes. These are the authentic chemical bricks of our new synthetic chemistry—the chemistry of rubber, of plastics, and of polymers of various degrees of molecular complexity. As will be seen in the sequel, such chemical bricks are of outstanding importance and value.

So, indeed, does cracking not only upgrade straight-run petroleum products, but also provides the starting-out material for synthesis, and, in fact, it is reasonable to envisage deliberate high-temperature cracking as a means of producing nothing else but reactive gases.

In recent years sheer thermal cracking has given place to catalytic pyrolysis in which, under the influence of contact media such as silica and certain silicates, and in the presence of free hydrogen under considerable pressure, a variety of operations proceeds; in effect cracking reactions can to a large extent be controlled and directed into chosen paths. In addition, straight-chain linear paraffins may be "cyclized" or converted into substituted aromatic hydrocarbons, with concomitant dehydrogenation. Isomerization may also proceed. Indeed, with specific catalysts such as boron trifluoride or aluminium chloride *n*-butane may be converted in good yield to *iso*butane, a reaction of considerable importance in the alkanation process (*q.v.*).

"*Destructive*" *Hydrogenation.*

In addition to the pyrolytic treatment of heavier hydrocarbon and the reforming of lighter material, should be mentioned two rather recent developments. Under conditions of catalysis at very high pressure (*e.g.*, 200 atm. of hydrogen) practically 100 per cent. yield of gasoline is obtainable from a heavy cracking stock. Furthermore, by varying temperature and catalyst, spirit of high aromatic content may be achieved. It will be seen that by such means the transition paraffin $\longrightarrow$ olefine $\longrightarrow$ *cyclo*paraffin $\longrightarrow$ aromatic is entirely feasible, and that, from a petroleum starting-out material, all and every type of hydrocarbon derivative can be synthesized.

Products.

Only the briefest reference can be made to the white spirits for paint manufacture, the range of kerosines for heating and lighting, from the familiar "paraffin oil" to the long-time burning oil used in lighthouses and railway signal lamps, to the range of gas oils used as fuel and for gas enriching, to the range of lubricants from light spindle oil to heavy steam cylinder stocks, to the soft waxes for match impregnation, high-melting waxes for candles, waterproofing, and, finally, to the asphaltic residue for road surfacing and construction. Table IX shows the main course of these operations and the subsequent treatment of the accompanying gases.

The story of the straight distillation products of crude oil could, if time or space permitted, be extended into many chapters: into the range of fuels for the light and heavy diesel engine (surely better called the compression-ignition engine); into the realms of mineral lubricating oil, with the manifold problems of viscosity–temperature relationships; of physical and chemical stability, of dewaxing, of addition compounds designed to lower very materially friction under excessively high bearing pressures; of solvent extraction that makes it possible to extract from any crude oil a lubricant of high efficiency and an extract of rather peculiar properties; of waxes of all degrees of melting points and consistencies and asphalts of all varieties of those qualities that make for the permanence of road surfaces. Such a story would be outside the limits of the present paper. But it must be recognized, however, that in their proper place all these problems are within the scope of the petroleum chemist.

TABLE IX.

Crude Oil ex Well
Stabilized Crude
Distillation
Paraffin Gases
Mainly C_1 to C_4
Whole range of Distillates, e.g.,
Petrol, White Spirit, Kerosines, Gas Oils,
Wax Distillates for Lubricants and
Pitch Residue
Amount of further
Paraffinoid Gases
Cracking and Reforming of
Selected Distillates
Pyrolysis for
Aromatic Hydrocarbons
Dehydrogenation to
Reactive Olefines
isoButane for
Alkanation
Isomerisation of n-butane
Cracked Spirit
Olefine Content of Cracked Gas
(C_3 to C_4)
Residues
Catalytic Polymerization
over Phosphates
Polymerization by Cold Sulphuric
Acid
Treatment with isoButane
(the Alkanation Process)
Motor Spirit of
High Octane Number
Selected Polymer
Cut
Diisobutylene
Other C_4 Olefine
Hydrocarbons
Hydrogenation
Hydrogenation
Polymerization
over Phosphates
Mixed iso-
Octanes
iso-Octane
High Octane
Motor Spirit
iso-Octane

Refining.

The chemical and physical refining of the crude cuts from mineral oil has naturally extended all the abilities of the scientific personnel of the industry. Few indeed of the raw products are usable as such; some, of course, by virtue of sheer costs cannot be further treated—most residue fuels, marine diesel oils, gas, oils and the like are put on to the market much in the form in which they left the stills. It is perhaps questionable whether or not refining has not overshot the mark. Consider, for example, the removal of sulphur derivatives from gasoline. Not so long ago a sulphur content of 0·01 per cent. was regarded as a reasonable figure. Egloff on many occasions has pointed out the futility of such a specification—in point of fact, it is only when the effect of certain thio-derivatives on lead tetraethyl is considered that a real case can be made out for reasonably complete sulphur removal. Again, in the refining of kerosine or lamp oil, due consideration must be given to the effect of deleterious compounds on the wick, on the chimney, on smokiness, and on combustion generally. A high degree of purity is likewise demanded for solvent oils, used, for example, in the paint and varnish industry. Very special considerations arise when lubricating oils are considered. These derivatives must possess chemical and physical stability in high degree, they must be characterized by a good viscosity index—that is to say, a flat temperature—viscosity curve—and ability to withstand higher and higher bearing pressures.

But it is at least important to decide *prima facie* what must and what must not be removed from a product to fit it for its purpose in our economic life—and it must be confessed that in the past far too much attention has been paid to appearance, colour, smell, and other purely æsthetic considerations.

Taking the individual products *seriatim*: Gasoline is entirely a motor fuel and its refining must be judged only from the point of view of its performance in the engine.

Clearly, colour and smell, and appearance are beside the point, except in so far as they indicate the presence of bodies that foul and corrode the engine and interfere with its efficiency. Because most gasolines are now "leaded" to increase efficiency, sulphur derivatives must be removed—this can be achieved in a variety of ways. These derivatives are hydrogen sulphide, mercaptans, and thio-ethers. Simple soda washing removes hydrogen sulphide and part of the lower mercaptans. Mercaptans are readily oxidized to disulphides, and rendered thereby odourless, but the total sulphur content remains. Solvent extraction by means of such bodies as salts of amino-acids definitely removes these substances, as does complete oxidation with alkaline hypochlorite. Where, however, lead tetraethyl is not used it is really quite immaterial whether sulphur is present or not. There is, however, another aspect of the refining of gasoline that becomes important when cracked spirits or blends thereof are considered. It may at once be agreed that cracked material is less stable than the straight-run product, not so much by its content of olefines, because these hydrocarbons are in effect as resistant to change as are the paraffins. It is rather the far more reactive compounds—probably diolefines—that

oxidize readily into gummy products. Such chain oxidations can be inhibited by the addition of quite minute quantities (0·005–0·01 per cent.) of anti-oxidants such as benzylaminophenol, the mixed cresols, quinol, xylenols, catechol, and certain fractions (*guiacol*) of wood tar. The net result is that such inhibited spirits withstand change for so long a storage period as a year.

The alternative process in the past was an intensive treatment with sulphuric acid, which not only brought about serious losses, since the harmless olefines were removed as well as the reactive hydrocarbons, but also was obviously a costly operation in terms of the reagent expended. So from the point of view of the refining of gasoline the essentials are: (1) removal of all sulphur derivatives if lead tetraethyl is to be added; (2) replacement of undue acid treatment by the addition of anti-oxidants. Questions of colour do not arise, since so much gasoline to-day is dyed.

The refining of kerosine is mainly concerned with burning properties and the removal of those bodies that cause charring of the wick, discoloration and fouling of the lamp-glass, and smokiness. The petroleum chemist is inclined to ascribe these defects to the presence of the thio-compounds, reactive unsaturated hydrocarbons, and aromatic derivatives. Again, of old, drastic acid treatment generally sufficed, but there were cases in which even excessive acid failed to yield a clear-burning kerosine. Such a case was found in Roumanian oil, but here a successful treatment was discovered by Edeleanu, who showed that extraction with liquid sulphur dioxide, owing to the preferential solubility of aromatic, unsaturated, and thio-derivatives, yielded a heavy separable extract, whereas a supernatant insoluble "raffinate" was formed of eminently excellent burning properties. Edeleanu treatment by "solvent extraction" has proved its worth for other petroleum derivatives than kerosine.

Brief reference must be made here to refining processes dependent on adsorption. For many years removal of colour from paraffin wax has been achieved by filtration through special varieties of animal charcoal—and, of course, other industries use this useful decolorant. But there are adsorbents of wider significance. Of such are ignited bauxite and a number of mineral clays such as floridin, tonsil, and the like. These materials not only remove colour, but also highly polar components of the crude distillates, sulphur derivatives, and, in general, the various deleterious bodies present in the unrefined fractions.

In a similar way high-grade light solvent oils, replacing, for example, turpentine, are marketed, and are entirely free from objectionable and reactive material.

Lubricating Oils.

Some attention must now be given to the refining of the heaviest fractions, which contain lubricating oils and solid waxes. These fractions come between the "white oils" and the asphaltic residues; if the crude oil is not asphaltic the whole residue may constitute a lubricating oil base.

Although every crude oil yields a fraction (or a residue) mainly composed of oils possessing the quality of lubricants or friction inhibitors—yet these cuts differ markedly one from the other. Some are, in the main, paraffinic, often containing solid waxes in suspension with correspondingly

high set points; others are chiefly of asphaltic origin. All contain oxidizable and reactive impurities. It has already been shown that stringent acid refining has been replaced by processes largely physical and, in fact, solvent extraction to remove unwanted components is now very intensively practised. Such solvents are phenol, dichloro-ethyl ether (chlorex), furfural, nitrobenzene, sulphur dioxide–benzol, and dimethyl formamide.

These solvents divide the crude lubricant into an unwanted extract (which, however, is likely to find commercial application by the very reason of its reactivity and particularly its oxidizability) and a "raffinate." Chiefly these two fractions differ in their viscosity–temperature relationships. The expression Viscosity Index (V.I.) has been coined to express this, and is based primarily on an arbitrary figure of 100 for paraffin base oil and of 0 for certain Californian asphaltic oils. It is, of course, clear that for the lubrication of the automobile engine an oil whose viscosity changes least from the starting-up temperature to that of normal working is most likely to be favoured by the driver.

Although in fact solvent extraction is widely used as a means of improving viscosity index, it is of interest to note that high pressure hydrogenation is also effective for this purpose. Here it should be indicated how slender is our knowledge of the molecular structure of these high-boiling and complicated hydrocarbons.

Reasonable surmise seems to show that highly condensed multinuclear systems are characteristic of asphalt base crude that have a low viscosity index—on the other hand, long side-chains attached to similar condensed systems have a high V.I., and are conveniently described as possessing a high degree of paraffinicity.

Lubricating oil stocks which are highly asphaltic can be freed of asphalt content by a preliminary treatment with liquid propane which precipitates resinous and pitchy materials.

It has been indicated that solvent extraction processes remove reactive material, and therefore the refined oils are less liable to deposit sludges and gums in service, but at the same time this intensive refining is just as likely to eliminate those polar bodies on which true lubrication depends, for modern ideas on the *rationale* of lubrication point to the fundamental idea that a dual system is involved, that of the lubricated surface and that of the lubricant itself. Polar bodies must be present to, in effect, unite with the rubbing surfaces, and so it has come about in cases where high pressures are involved reactive bodies of high polarity are deliberately added to the refined oil, which becomes merely the carrier. Such bodies may contain chlorine, phosphorus, and sulphur.

Synthetic Lubricating Oils.

Some advances have been made in the field of synthesis of lubricating oils, and more are likely to emerge in the future. Just as with other artificially produced fractions, it appears probable that specific properties can best be met by creating specific hydrocarbon entities. So far as our knowledge goes, the essential components of mineral lubricants are long side-chains attached to ring structures, a combination of catenary and cyclic molecules. Empirically, something has been done in the direction of polymerization of olefinic bodies under the influence of aluminium

chloride. Incidentally, some of these polymers which may possess a molecular weight of 20,000 have a remarkable effect on viscosity index.

Curiously enough, such high-molecular-weight hydrocarbons—usually synthesized from a long side-chain attached to an aromatic nucleus—have been applied to the problem of lowering the setting point of lubricating oils derived from paraffin containing crudes. These substances apparently operate by being selectively adsorbed on the growing faces of the wax crystals, stopping the development of large impermeable units.

Utilization of Petroleum Gases.

In what follows, main consideration will be given to the development of the various methods of utilizing petroleum gases, the very bricks of the new synthetic oil industry.

The earliest attempts to utilize the lower paraffin hydrocarbon depended on drastic thermal treatment. This operation was known as pyrolysis. Methane, unfortunately, proved most recalcitrant and yields were low, although mainly of an aromatic nature. At the same time reference should be made to the vastly important formation of acetylene therefrom. In recent years the process has been confined to the higher homologues. Fig. 11 shows a typical set up, in which the higher paraffinic gases (C_3 and C_4) are heat-treated. Mention should be made here, however, of the partial pyrolysis of these gases leading to the production of the corresponding olefines. Such dehydrogenation is effected by the joint impact of heat and catalysis.

Reverting, however, to the gases produced in the cracking and reforming processes, a typical analysis shows:

TABLE X.

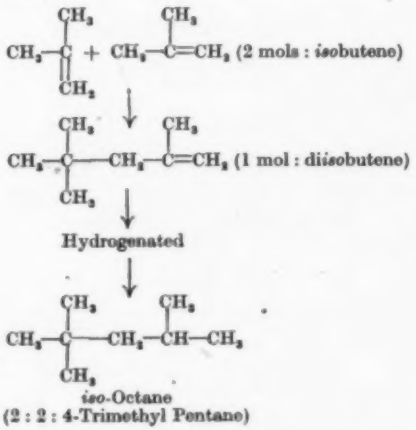
	Mol., per cent.
CH_4	58
C_2H_4	7
C_2H_6	13
C_3H_8	11
$C_4H_8 + C_4H_{10}$	5

From the point of view of refinery procedure, these are concentrated into C_3 and C_4 fractions (the lighter gases C_1 and C_2 at the moment being of fuel value only, although this is obviously only a temporary phase). Clearly the last to be utilized on a vast commercial scale will be methane, and this amounts to something of the order of 10,000,000 tons per annum from petroleum sources alone. It is on the C_4 fraction, however, that most work has been done. This contains *n*-butane, *iso*butane, the two normal butenes and *iso*butene in proportions that vary with the cracking conditions. Also present is butadiene (under high-temperature cracking conditions particularly—the so-called vapour-phase process).

An early commercial operation was concerned with *iso*butene, and it must be remembered that in this connection "early" means only a few years ago. When treated with 65 per cent. sulphuric acid at ordinary temperatures this hydrocarbon is absorbed and converted into *tert.*-butyl alcohol.

On raising the temperature of the acid alcohol mixture to 100° C. a split takes place—" nascent " *iso*butene is regenerated and immediately forms the dimer and, to a less extent, the trimer. Schematically, the change is as follows, there being a final hydrogenation process leading to *iso*-octane :

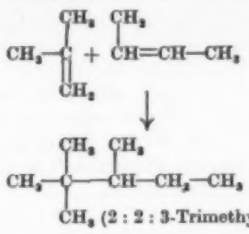
Dimerization of isobutene.



In Fig. 12 is shown a unit plant for polymerizing *iso*butene ; Fig. 13 illustrates the hydrogenation plant for the last stage.

The remaining butenes must now be considered. Using hot sulphuric acid, a co-polymerization of the total butenes ensues.

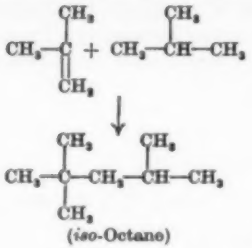
Co-polymerization of iso*Butene and* n-*Butene, followed by Hydrogenation.*



Actually there is a whole range of catalysts that bring about the polymerization or the co-polymerization of these olefines. Chief amongst these is a variety of phosphates, *e.g.* hydrogen, copper, and cadmium, and further various well-known naturally occurring compounds of alumina and silica.

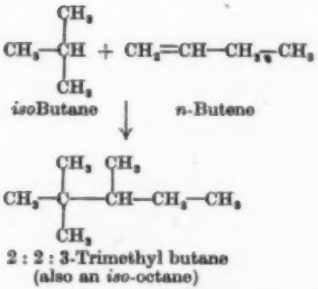
A further development arose when it was discovered that *iso*butane would smoothly unite in the presence of sulphuric acid or of hydrogen fluoride with the butenes and yield *iso*-octane in one operation.

Addition of iso*Butene to* iso*Butane.*



(*iso*-Octane)

and further:



*iso*Butane | *n*-Butene

2 : 2 : 3-Trimethyl butane
(also an *iso*-octane)

This reaction, not yet quite fully explained, and possibly not quite developed to the full, is one of the most elegant syntheses accomplished in the field of petroleum chemistry. It is conveniently termed "alkanation," although the expression alkylation is perhaps more commonly used, especially in America.

The alkanation reaction has been fully studied in the case of *iso*butane, coupled with the two normal butenes, with di*iso*butene and, in fact, with the whole C_4 cut. Curiously enough, if the end major product (*iso*-octane) is similarly treated with sulphuric acid, there appears, in effect, to occur a reverse reaction, and the final products are similar to those encountered in the initial reactions.

The union of two hydrocarbons, one containing the tertiary carbon atom characteristic of *iso*butane and the other an olefine, is, as just explained, carried out in the presence of a catalyst. But by the mere impact of temperature and pressure *iso*butane will add on ethylene to yield neohexane, an excellent anti-knock fuel.

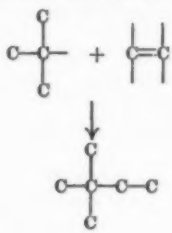


FIG. 1.

A HIGH-PRESSURE WELL-HEAD GAS SEPARATOR.

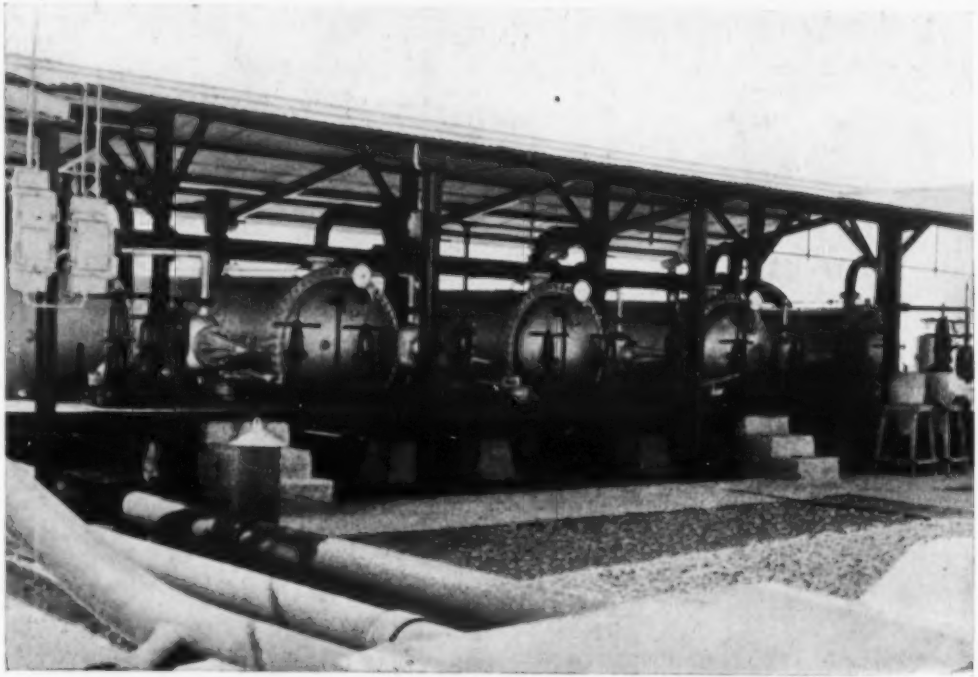


FIG. 2.
MULTI-STAGE GAS SEPARATOR.

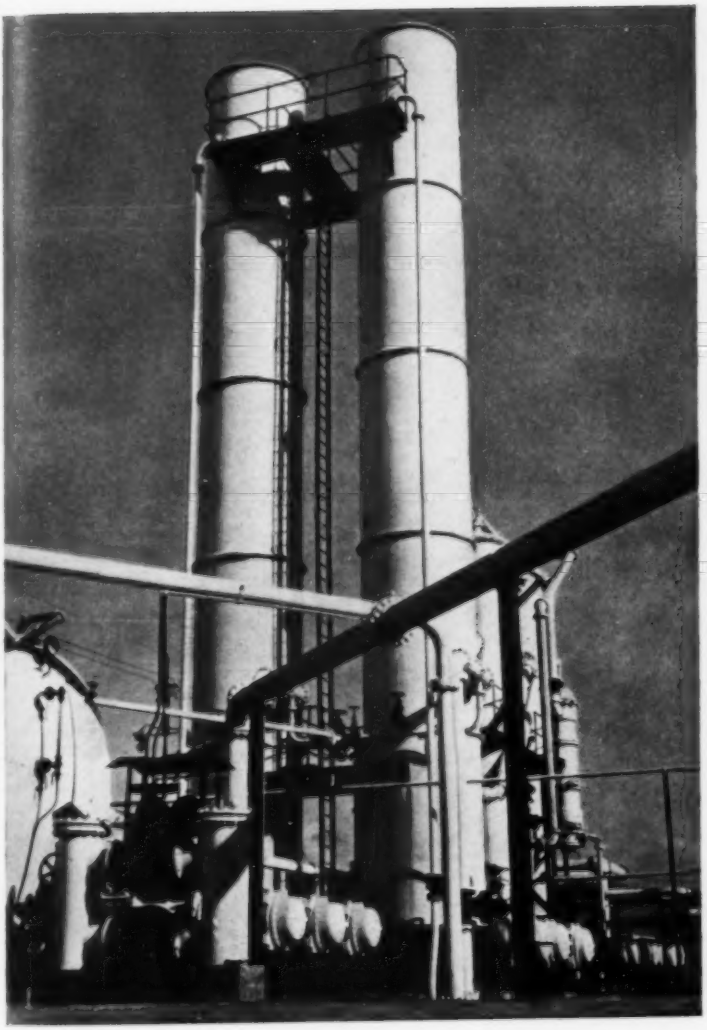


FIG. 2.
MULTI-STAGE GAS SEPARATOR.

FIG. 3.
TOWERS IN A GAS-ABSORPTION PLANT.

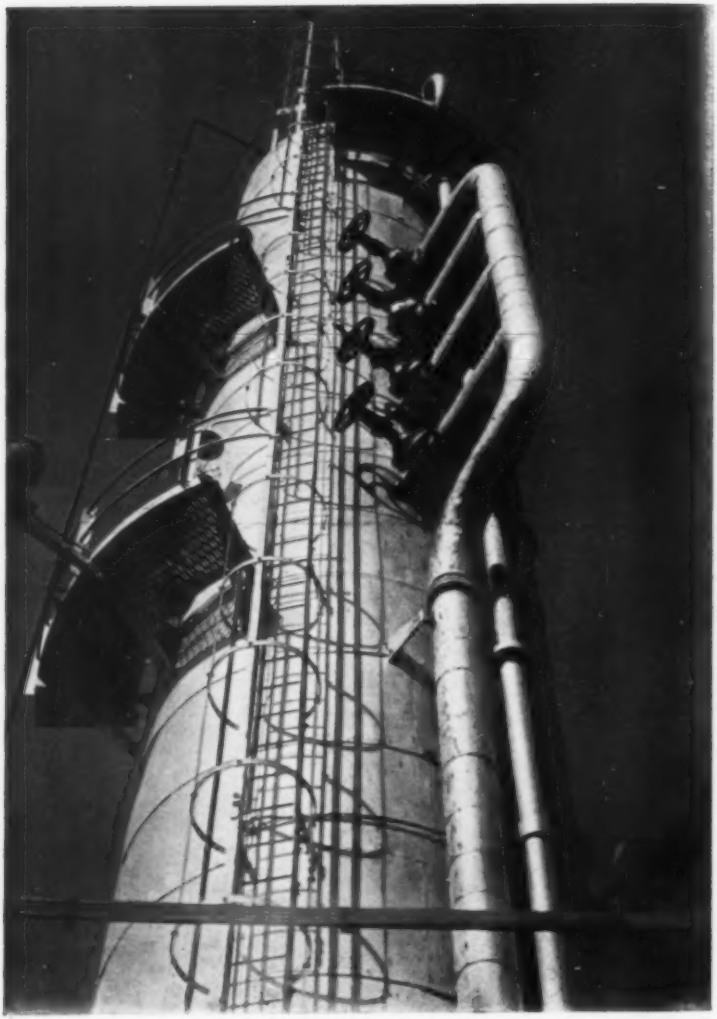


FIG. 4.

COLUMN OF A STABILIZING UNIT.

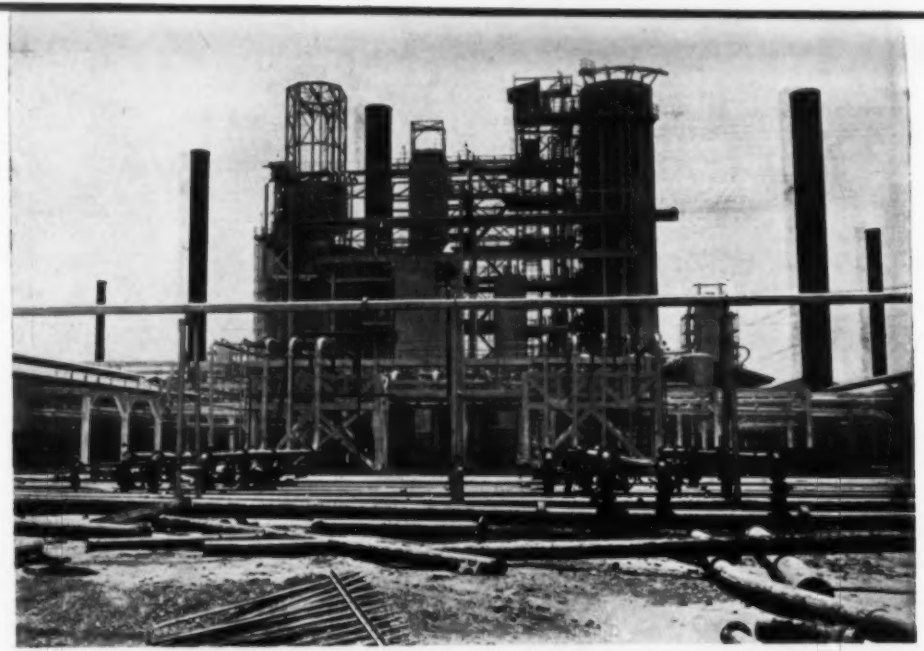


FIG. 5.

A MODERN DISTILLATION UNIT (3,000,000 TONS OF CRUDE PER ANNUM).

The column in the middle is the primary flash tower, on the right is the main tower that removes the white oil, and on the left is the vacuum column. The height of the main tower is well over 100 feet, its diameter 20 feet, and it possesses 25 decks.

FIG. 6.

A SERIES OF THERMAL CRACKING UNITS.

FIG. 6.

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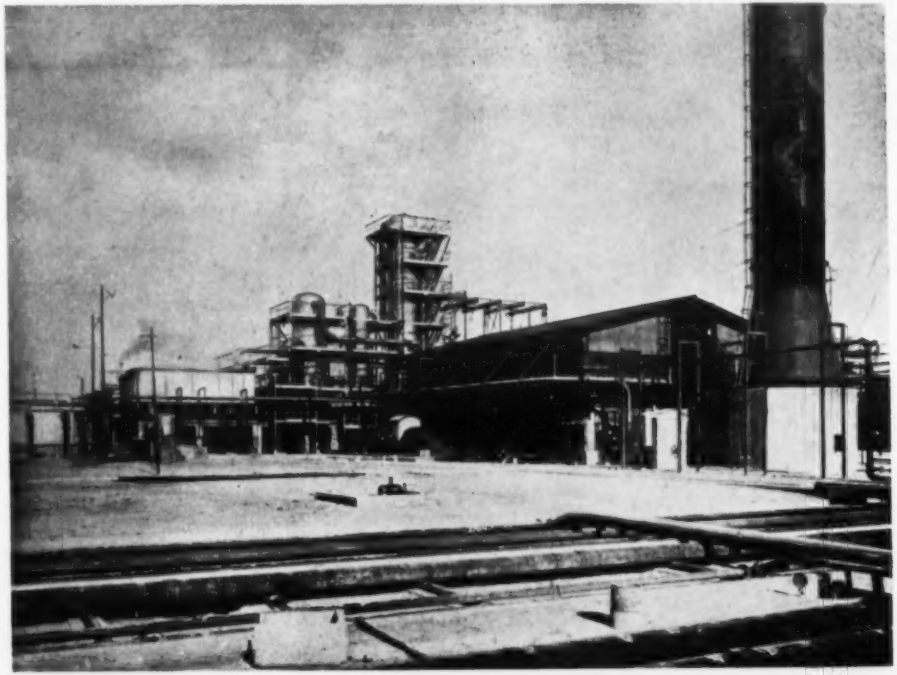


FIG. 7

A NAPHTHA REFORMING UNIT.

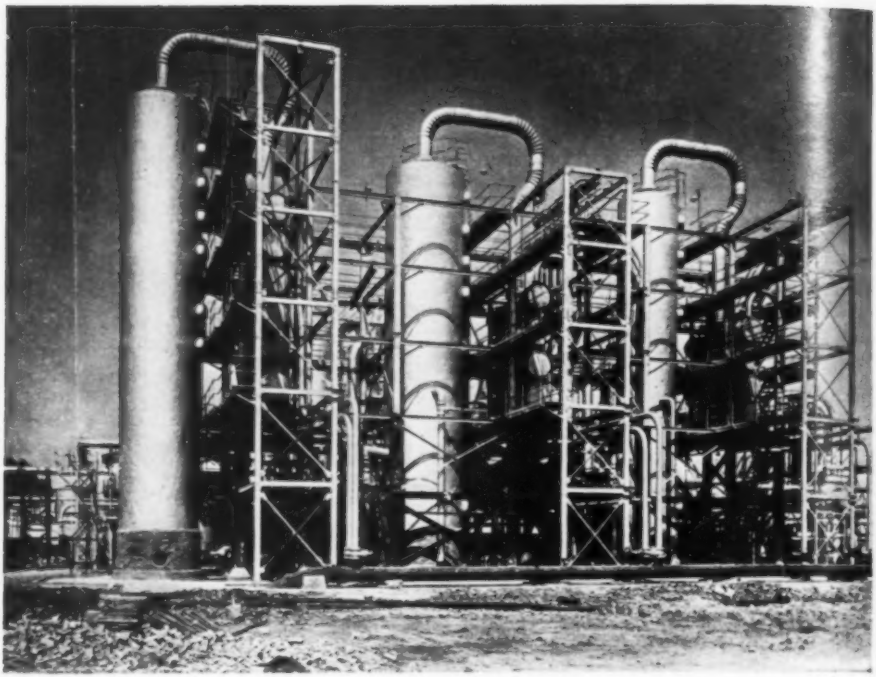


FIG. 8.

A RE-RUN UNIT FOR LIGHT PRODUCTS.

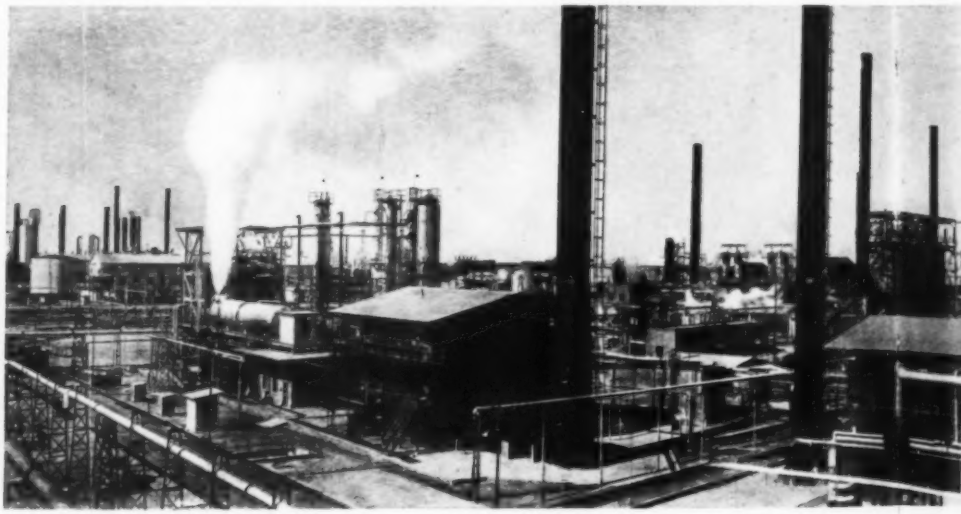


FIG. 10.

A PANORAMA OF A MODERN REFINERY SHOWING P

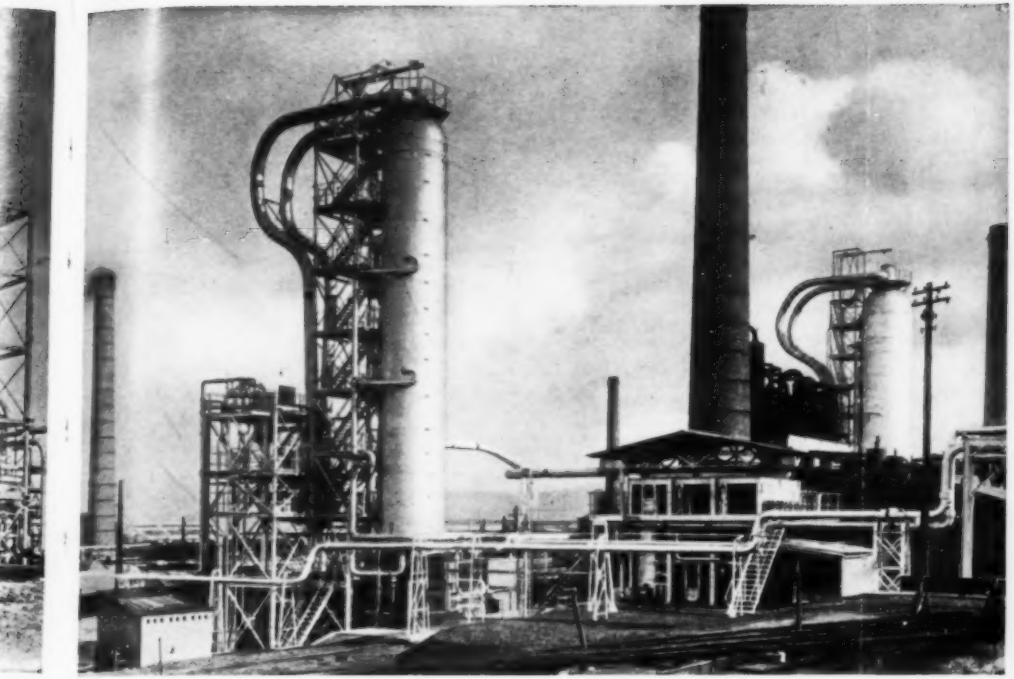


FIG. 9.

HIGH VACUUM DISTILLATION UNIT FOR LUBRICATING OILS.

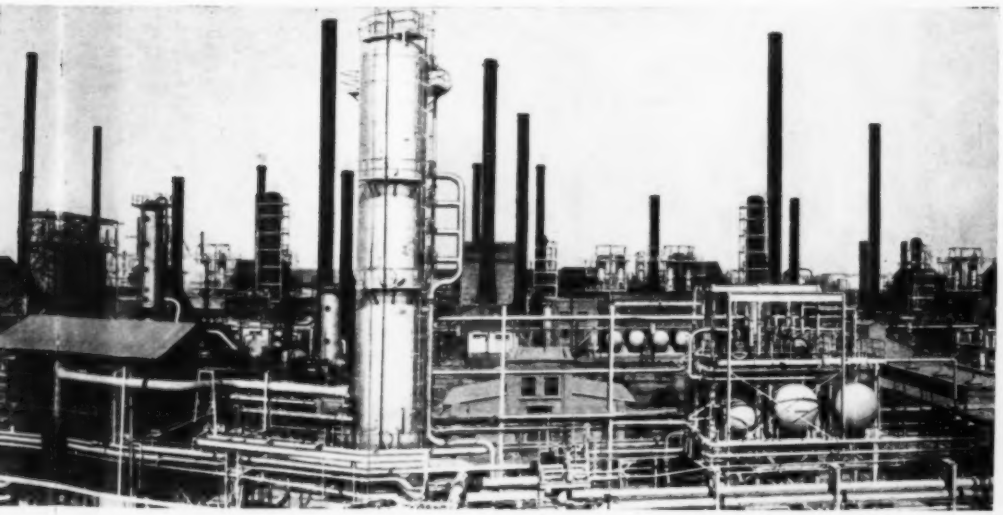


FIG. 10.

ERY SHOWING PART OF THE GAS UTILIZATION SECTION.

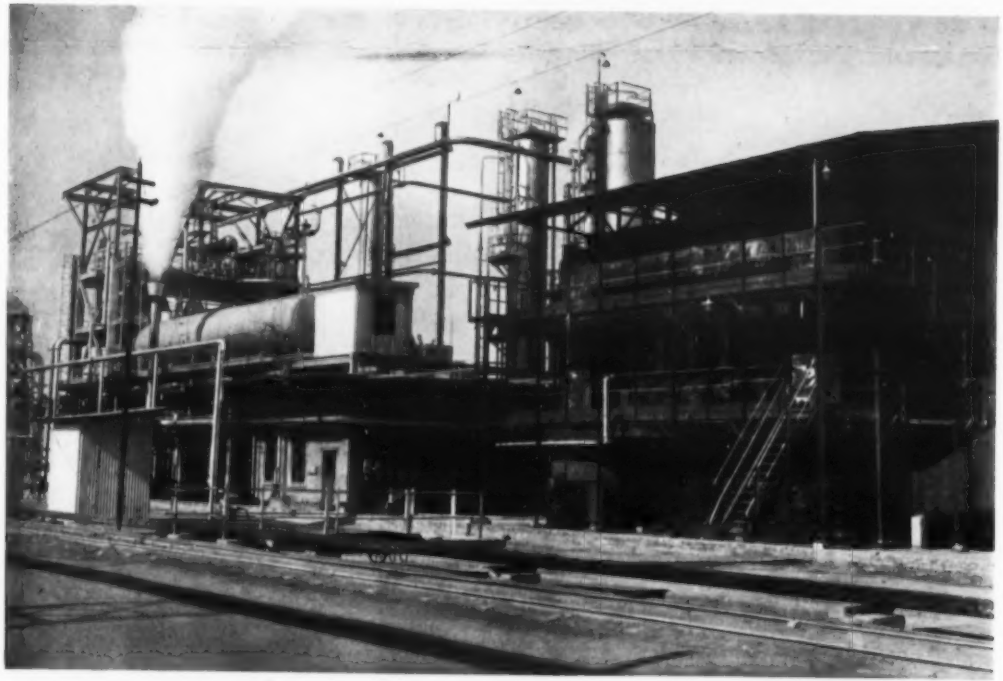


FIG. 11.

PYROLYSIS PLANT SHOWING FURNACE CONSTRUCTION.

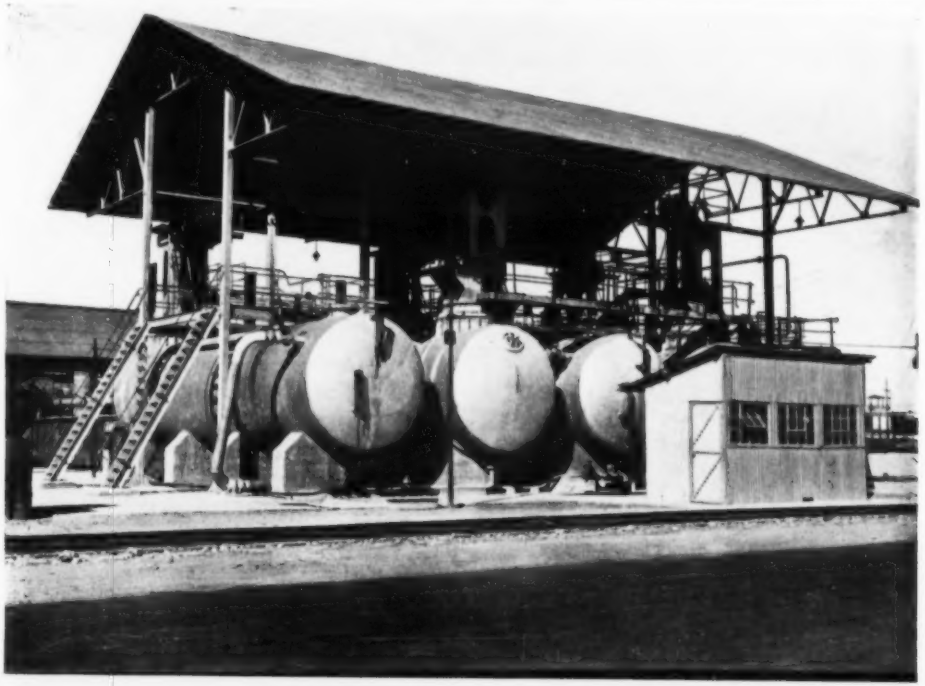


FIG. 12.

REACTION VESSELS FOR THE MANUFACTURE OF DI*iso*BUTENE.

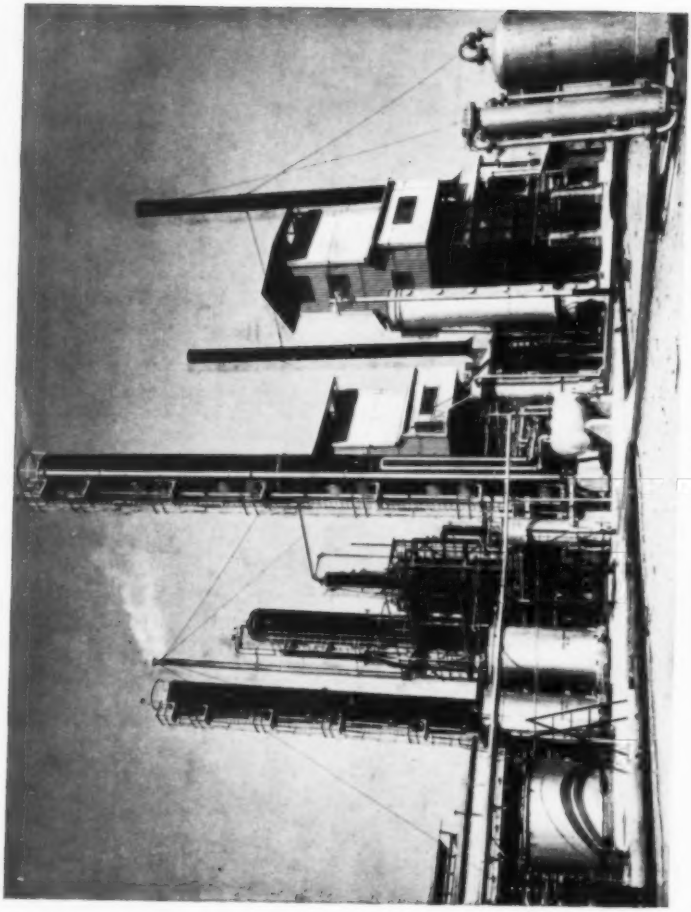


FIG. 13.

HYDROGENATION UNIT FOR THE CONVERSION OF *DIISOBUTENE* TO 2 : 2 : 4-TRIMETHYL PENTANE.

To recapitulate:

2 molecules *iso*butene ⟶ di*iso*butene ⟶ *iso*-octane
n-butene + *iso*butene ⟶ co-dimer ⟶ *iso*-octanes
*iso*butene, *n*-butenes } + *iso*butane ⟶ *iso*-octane.

Clearly the last operation gives the greatest yield of *iso*-octane from the C_4 fraction, and that in one operation.

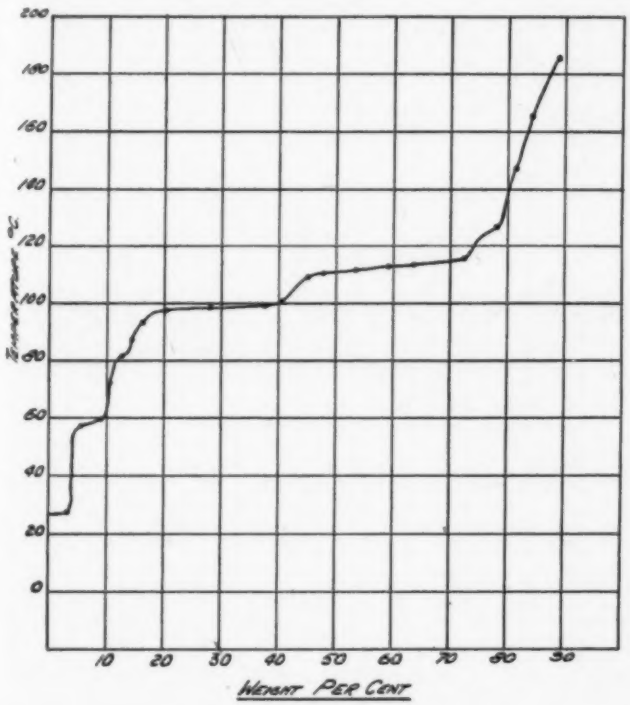


FIG. 14.

FRACTIONATION CURVE FOR THE PRODUCT BUTENE–*iso*BUTANE.

It is of some interest there to indicate how a careful fractionation of, for example, the crude product 2 : 2 : 4-trimethylpentane prepared from *iso*butene and *iso*butane shows not only the preponderance of the *iso*-octane, but also other accompanying hydrocarbons and how, similarly, the back reaction between sulphuric acid and *iso*-octane itself yields a material the distillation curve of which may well be compared with the former graph. (Figs. 14 and 15.)

It is important at this stage to stress the characteristic behaviour of the tertiary carbon atoms in *iso*butane and its allies, not dissimilar from

the reactivity of the carbon atoms in the aromatic nucleus. Normal butane does not react in the same way. Fortunately, however, normal butane can be isomerized into *iso*butane, and this operation is brought about by catalysis with aluminium trichloride or boron trichloride supported on various carriers; such procedure is obviously a matter of great importance in the syntheses briefly outlined above.

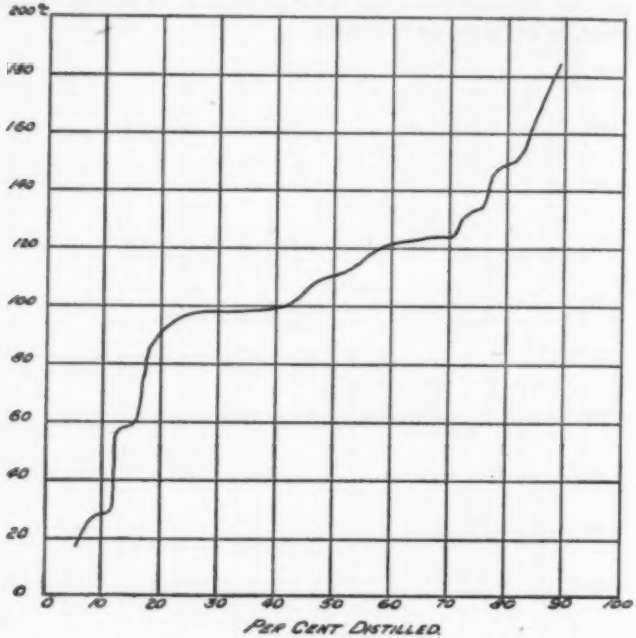


FIG. 15.

FRACTIONATION CURVE FOR THE BACK REACTION PRODUCT OF SULPHURIC ACID–*iso*-OCTANE.

The hydrocarbon products hitherto described may fairly be called motor fuels. But there is a vastly important field of synthesis leading to a remarkable out-turn of organic materials of the most diverse nature—and broadly all these are derivatives of the olefines. As was shown earlier in this lecture the unsaturateds are readily produced by the dehydrogenation of the paraffins over various catalysts.

Although, without doubt, the principal use of petroleum will always be as a source of fuel, lubricants, and road-surfacing asphalt, chemical developments in recent years have opened up entirely new vistas of usefulness. The chemist views petroleum not only as a mixture of petrol, kerosine, etc., but as an assembly of carbon and hydrogen atoms put together by Nature like so many bricks to form edifices of certain specific designs known as paraffins, naphthenes, and aromatics. He realizes, moreover, that it is possible to break down these structures which may

be useful only as fuel, into their component bricks, and with these bricks to reconstruct new edifices of a design and pattern suitable for quite different purposes. For example, by demolition of heptane, one of the hydrocarbons in petrol, and the regrouping of the carbon and hydrogen it contains, it is entirely possible to build toluene for explosives or styrene for flexible glass or butadiene for synthetic rubber.

By combining these derived hydrocarbons with oxygen there can be made alcohol, glycerol, and acetaldehyde, the parent materials for the newest types of synthetic textiles, ornamental moulded plastics, resins, paints and varnishes, synthetic rubbers, flotation agents, insecticides, and detergents. In effect all the well-known products known of old as originating from coal tar are obtainable from petroleum bricks.

The chemical rebuilding of petroleum is not a new and revolutionary development. It had its birth many years ago when unwanted heavy oil was " cracked " to break down its molecular structure, and so to create burning oil and, at a later date, petrol. Still more recently the petroleum industry began to develop the chemical synthesis of particular desired materials from the disrupted fragments of hydrocarbons which so far had been waste by-products. From cracker gases *iso*butene was isolated and by a sequence of chemical treatments converted into *iso*-octane. Polymerization, alkanation, hydrogenation, cyclization, aromatization—all the chemical armoury was brought into commission to break down, re-arrange and rebuild less valuable hydrocarbons into hydrocarbons of greater economic and practical value.

So far these new materials have been mainly employed as high-grade fuels to improve or to replace the natural product, but to-day an infinitely wider field of opportunity is open. Hitherto most industrial commodities, apart from metals, have been of vegetable or animal origin; one can instance textiles, paints, varnishes, solvents, dyes, drugs, rubber, plastics —the list is endless. To-day, a great and rapidly expanding chemical industry is being developed from petroleum, whereby every one of these various classes of commodities is being manufactured from mineral oil, and one cannot doubt that this industry, still, as yet, in its early childhood, is destined to expand surely and rapidly to a scale and scope almost impossible to envisage.

Synthetics.

Ethyl alcohol has been in commercial synthetic production for a decade or more, and absorption of ethylene in sulphuric acid has been invariably the favoured process. It is significant, however, that the direct hydration of the hydrocarbon is attracting attention; and, further, as B. T. Brooks has pointed out, the use of relatively dilute sulphuric acid under elevated conditions of temperature and pressure leads to a continuous production of alcohol, with avoidance of reconcentration.

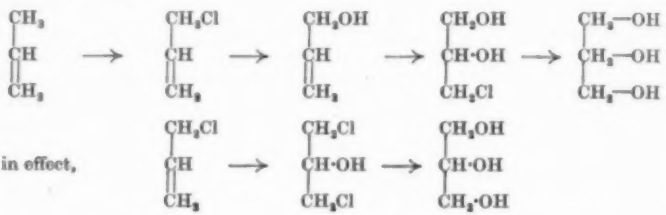
Oxidation of ethanol to aldehyde, the condensation of the latter to aldol, and subsequent dehydration to butadiene are preliminaries in the synthesis of rubber.

Clearly these derivatives depend on a source of reasonably pure ethylene, and this, in turn, depends on the effective separation of the constituents of cracked gases.

To some extent, and for certain specific purposes, ethylene may be separated from accompanying propylene by its lower solubility in sulphuric acid—it being, of course, premised that a separation between the C_1–C_2 and the C_3–C_4 groups has been effected by fractionation of the cracked gases under pressure.

The use of ethylene as an intermediate in the manufacture of mustard gas and in the synthesis of lead tetraethyl might be mentioned at this stage.

Propylene is readily converted into *iso*propyl alcohol, a useful solvent, *via* propyl hydrogen sulphate, and the alcohol itself passes by catalytic dehydrogenation into acetone. Obvious steps lead to ketene and to acetic anhydride. An extremely interesting observation by E. C. Williams has lead to the commercial synthesis of glycerol and β-methyl glycerol. Alkyl chloride is formed by the chlorination of propylene at high temperatures. Hydrolysis of this leads to alkyl alcohol. After hydrochlorination the chlorhydrin is produced, which, with alkali treatment, yields ultimately glycerol:



Similar reactions proceed in the case of *iso*butene.

The importance of this set of reactions lies, of course, in providing a source of glycerol competitive with the usual hydrolysis of fats.

Further derivatives from propylene and prepared by well-known methods are: Acetone, *iso*propyl ether, methyl ethyl ketone, *tert.*-butyl alcohol, allyl alcohol, methallyl alcohol, acrolein and epichlorhydrin. Of special interest to the petroleum chemist is di*iso*propyl ether—known recently to be a potent anti-knock material.

*iso*Butene has already been mentioned as the source material of di-*iso*butene which on hydrogenation yields *iso*-octane. But on chlorination it provides methallyl chloride, the homologue of allyl chloride. From methallyl chloride proceeds the alcohol and the oxidation product methacrolein, that in turn can be oxidized to *iso*butyric acid.

Amongst the earliest successful attempts to develop the synthesis of derivatives of petroleum was the production of ethylene glycol *via* the chlorhydrin readily obtained by the reaction between ethylene and chlorine water. Glycol soon attained a commanding place as the most convenient and economical "anti-freeze," and still retains that position. To-day the more important of the glycol series include diethylene glycol, ethylene glycol methyl ether (methyl cellosolve), ethylene glycol butyl ether (butyl cellosolve), diethylene glycol methyl ether (methyl carbitol), diethylene glycol ethyl ether (carbitol), dioxan, dichloroethyl ether (chlorex—an important solvent in the refining of lubricating oil fractions), ethylene oxide, ethylene dichloride, ethylene chlorhydrin, the ethanolamines, and ethylene-

diamine. Brief reference also may be made to the nitrated glycols as explosives. The dehydrogenation of *iso*propyl alcohol to acetone is now an accomplished fact, and new low cost levels for acetone have been achieved. Acetone may be condensed to diacetone alcohol, and this dehydrated to mesityl oxide, and then further hydrogenated to methyl *iso*butyl ketone. Also well known in the reactivity of these materials is the pyrolysis of acetone to ketene :

$$CH_3{\cdot}CO{\cdot}CH_3 \longrightarrow CH_2 = CO + CH_4$$

Ketene with acetic acid yields acetic anhydride—an outstandingly important intermediate in synthetic chemistry. Furthermore, ketene readily polymerizes to diketene, and this yields in turn aceto-acetic esters.

The alkyl halides deserve a brief mention. Ethyl chloride is a very important intermediate in the production of lead tetraethyl. It may be synthesized *via* ethylene and hydrogen chloride. Ethylene dichloride made directly from ethylene, and the halogen is used in the manufacture of thiokol rubber by interaction with sodium polysulphides. Specially may be mentioned the chlorinated pentanes which have been for some years the source of material for the production of amyl acetates and alcohols as solvents.

Ethyl chloride, reacting under the influence of such catalysts as aluminium chloride on benzene, yields ethyl benzene, which is clearly the intermediate in the formation of styrene, and hence the styrene resins and rubbers.

The chlorination of propane under pressure giving (1 : 3)-dichloropropane is the first step to *cyclo*propane—a useful anæsthetic. Derivatives such as *tert.*-butyl phenol are of interest in the manufacture of specialized resins, and similarly *tert.*-amyl alcohol readily alkylates phenol yielding *tert.*-amyl phenol.

Of somewhat more recent interest is the manufacture of detergents. A chloro-derivative of a long-chain paraffin is converted into an alkyl-aryl compound, which on sulphonation yields an acid. The sodium salt is found to possess excellent wetting properties. In general, all detergents comprehend a hydrophobic long carbon chain, together with a hydrophilic group, usually a sodium sulphonate.

Mention should here be made of the co-polymerization of dienes and olefines (both simultaneously produced in the high temperature cracking of petroleum) under the influence of, for example, aluminium or boron trichloride. For example, *iso*butene itself yields a series of highly polymerized hydrocarbons, from liquid material of use in improving the viscosity index of a mineral lubricating oil to a material of very great molecular weight, resembling rubber itself, and known as Vistanex.

It has already been indicated that the paraffins *tel quel* are not as reactive as the olefines, nevertheless they are of considerable interest. Methane, for example, yields the *mono* to the *tetra* chloro- (and nitro-) derivatives. The C_5 chloro-derivatives are source material for alcohols, esters, and amines. Further, by oxidation the paraffins are starting-out material for alcohols, aldehydes, ketones, and fatty acids, soaps, edible glycerides, detergents, and wetting agents.

The pyrolysis of methane to acetylene should be stressed. It is not

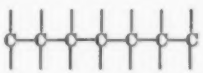
generally known that natural gas, the world over, represents about ten million tons a year of available hydrocarbon (mainly methane), most of which is lost or burnt at the fields and refineries as fuel. From this vast quantity it is reasonable to assume that the production of not only acetylene, but also aromatic hydrocarbons will be found profitable.

And, of course, from acetylene are derived acetic acid, a wide range of polymers and plastics. What is really important here is that high-temperature cracking or pyrolysis of any petroleum fraction from methane to hydrocarbons of high molecular weight yields in effect a "synthetic" coal tar, and that all the well-known derivatives thereof—dyes, solvents, resins, plastics, explosives, detergents, and the like—are equally producible and obtainable from mineral oil, and obviously in greater quantity and more diverse in application.

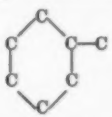
It has already been pointed out that the *iso*-paraffins are more reactive than their normal isomers—and it has been shown that only *iso*butane reacts with the butenes to form octanes by addition. Reaction of the higher normal paraffins with aluminium chloride as a catalyst brings about a substantial conversion into the reactive tertiary carbon derivative. It is possible that under conditions of high-temperature cracking, such isomerization may proceed normally. True it is that the normal occurrence of, *e.g.*, *iso*butane in the natural gas is insufficient to convert the whole of the butenes in the cracked gases corresponding to the ordinary cracking procedure in a modern refinery without the isomerization process—now becoming an integral part of refinery operation.

Cyclization.

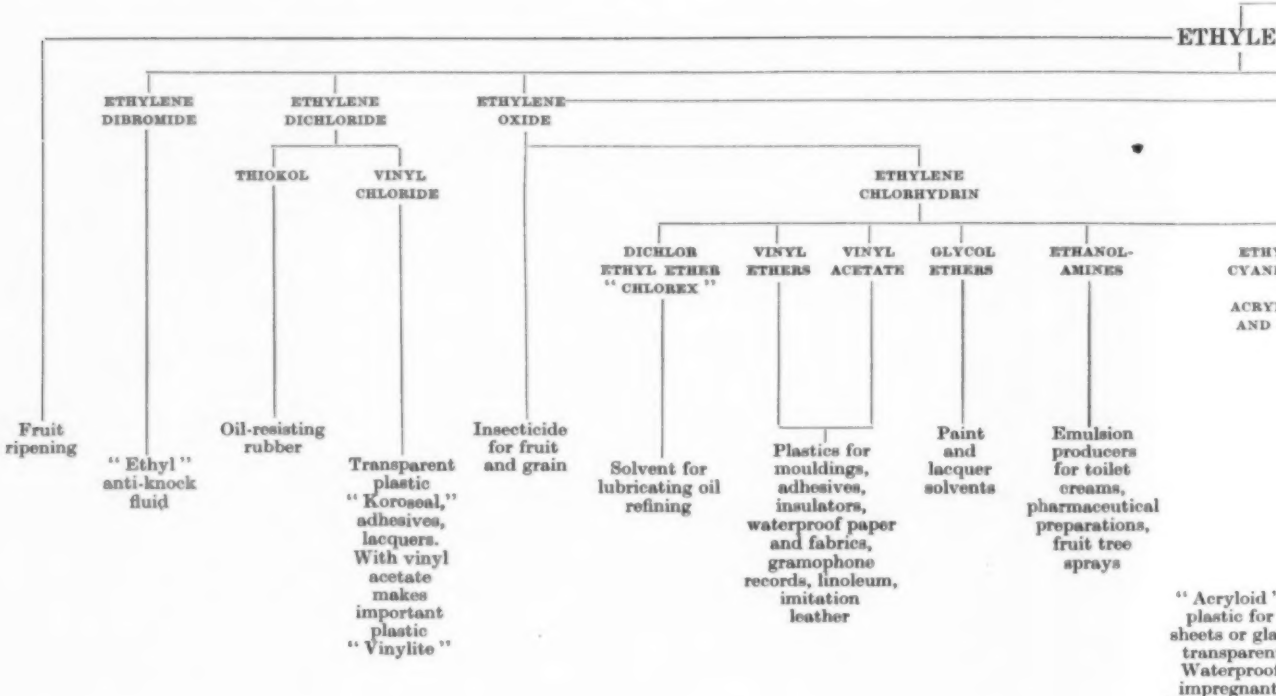
It has already been indicated that meticulously accurate fractionation of the low-boiling components of motor spirit is likely to result in a division of the raw material to high octane fuels such as *iso*pentane, methyl*cyclo*-pentane, and the like, from the thoroughly bad pro-knock fuels like *n*-hexane and its homologues—fit, of course, only for cracking (reforming) and cyclization. This latter process needs some elucidation. It is clear that *n*-heptane, for example:



tends to form a ring structure by elimination of hydrogen.



Under strenuous conditions of temperature, aided by catalysis, normal heptane loses hydrogen and yields methyl *cyclo*hexane—which again will give toluene on further loss of hydrogen. Such are the consecutive processes of cyclization and aromatization. When it is realized that *n*-heptane is one of the worst pro-knocks, whilst the *cyclo*paraffin methyl-*cyclo*hexane is rated far higher in the scale, and toluene even higher still, it is clear that these processes are of vast importance in the industry.


ETHYLE
ETHYLENE DIBROMIDE
ETHYLENE DICHLORIDE
ETHYLENE OXIDE
THIOKOL
VINYL CHLORIDE
ETHYLENE CHLORHYDRIN
DICHLOR ETHYL ETHER "CHLOREX"
VINYL ETHERS
VINYL ACETATE
GLYCOL ETHERS
ETHANOL-AMINES
ETHY CYAN
ACRY AND
Fruit ripening
"Ethyl" anti-knock fluid
Oil-resisting rubber
Transparent plastic "Koroseal," adhesives, lacquers. With vinyl acetate makes important plastic "Vinylite"
Insecticide for fruit and grain
Solvent for lubricating oil refining
Plastics for mouldings, adhesives, insulators, waterproof paper and fabrics, gramophone records, linoleum, imitation leather
Paint and lacquer solvents
Emulsion producers for toilet creams, pharmaceutical preparations, fruit tree sprays
"Acryloid" plastic for sheets or gla transparen Waterproo impregnant leather, wood floor tiles, lacquers an Among the grade plastics with Vinyl

SYNTHETIC PRODUCTS FROM THE CRACKING OF

PETROLEUM

GASES

HYDROGEN	ETHYLENE
METHANE	PROPYLENE
ETHANE	BUTENES
PROPANE	BUTADIENE
BUTANE	

—ETHYLENE— <— (dehydrogenation) <—ETHANE

—GLYCOL

ETHYL

ETHYLENE CYANHYDRIN

ACRYLIC ACID AND ESTERS

"Acryloid" transparent plastic for safety glass sheets or glass substitute; transparent mouldings. Waterproof covering or impregnant for textiles, leather, wood. Insulators, floor tiles, adhesives, lacquers and varnishes. Among the chief of high-grade plastics in conjunction with Vinyl compounds

Anti-freeze, aeroplane radiators

GLYCOL DINITRATE

Safer alternative explosive to nitroglycerol

GLYCOL STEARATE

Plasticiser for lacquers and plastics

GLYCOL PHTHALATE

Plasticiser for resins and plastics

GLYCOL METHYL ETHER

"METHYL CELLOSOLVE"

GLYCOL ETHYL ETHER

"CELLOSOLVE"

Solvents for paints and lacquers and varnishes

DIETHYLENE GLYCOL

Non-freezing liquid for hydraulic brakes

DI-E.G. DINITRATE

Explosive safer than nitroglycerol

DI-E.G. ETHYL ETHER "CARBITOL"

"CARBITOL" ACETATE

Solvent for lacquers and varnishes

TRIETHYLENE GLYCOL

Plasticiser for plastics and lacquers

ETHYL ETHER

Solvent for varnish pharmaceuticals, and essences; fuel; raw material for many chemicals, dyes, etc.; preservative; antiseptic

Solvent for oils, perfumes and essences; anæsthetic

ETHYL CHLORIDE

Refrigerant, Anæsthetic (local), Dyestuff intermediate

LEAD TETRAETHYL

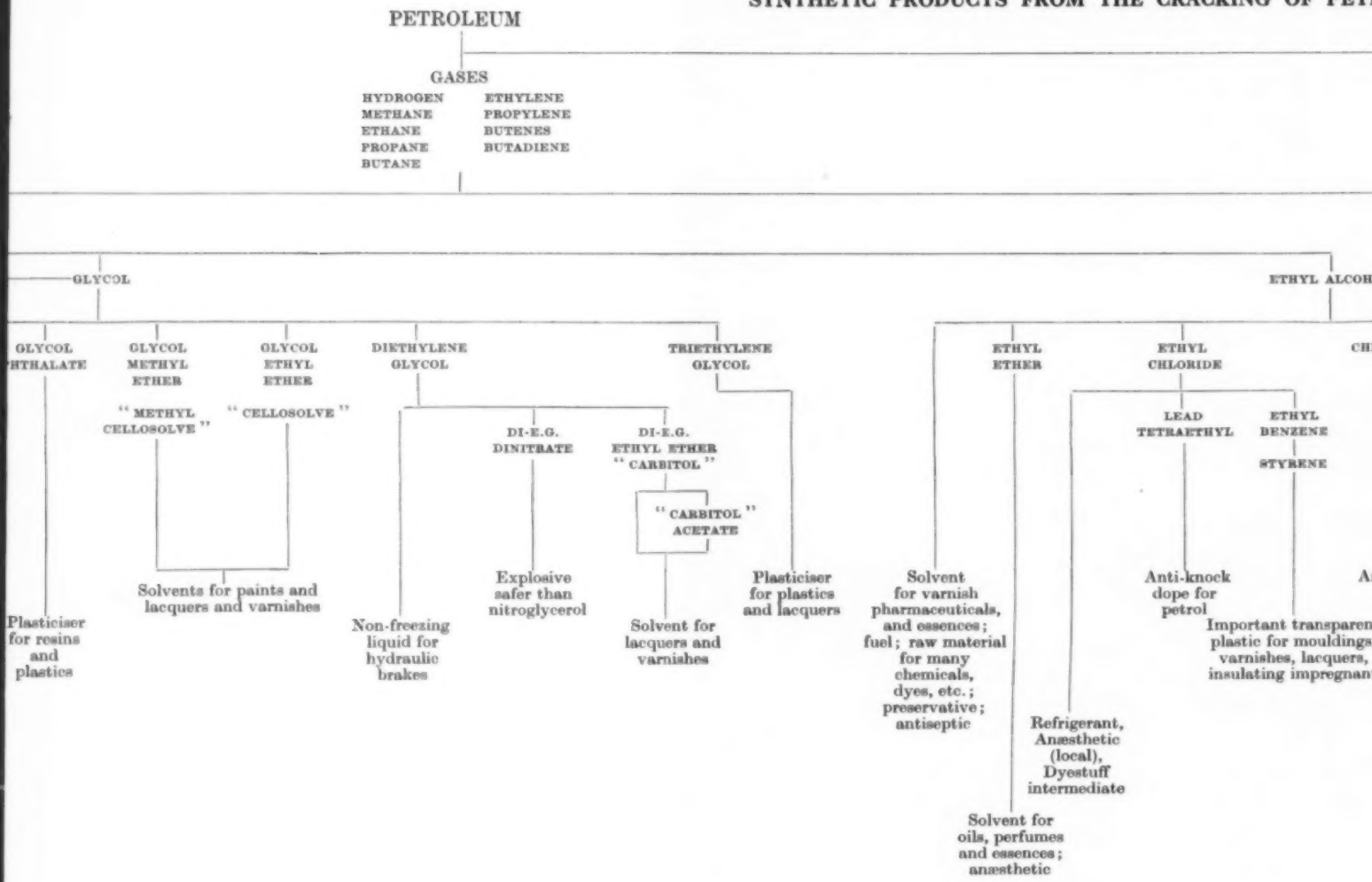
Anti-knock dope for petrol

ETHYL BENZEN

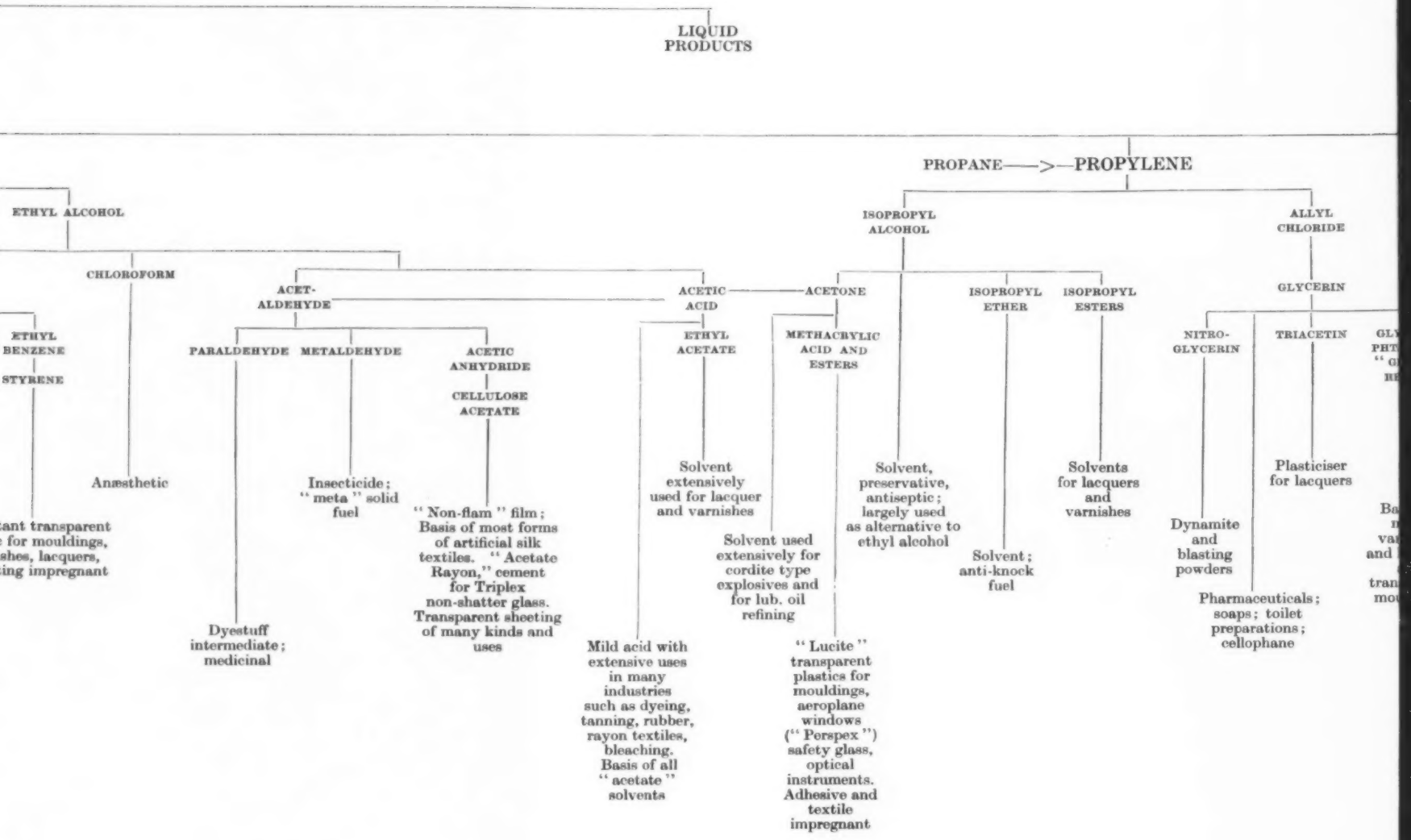
STYREN

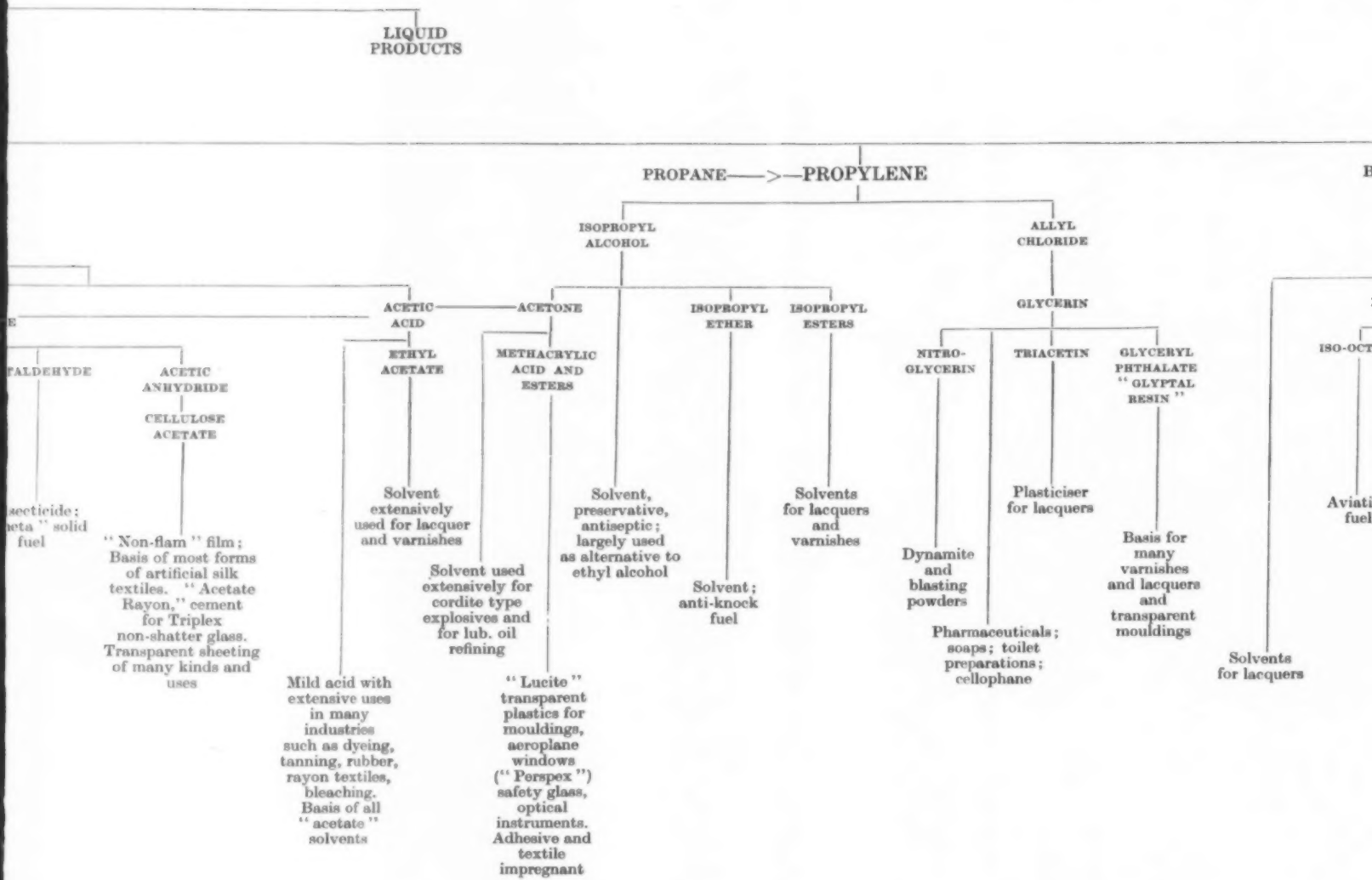
Important tra plastic for mo varnishes, la insulating imp

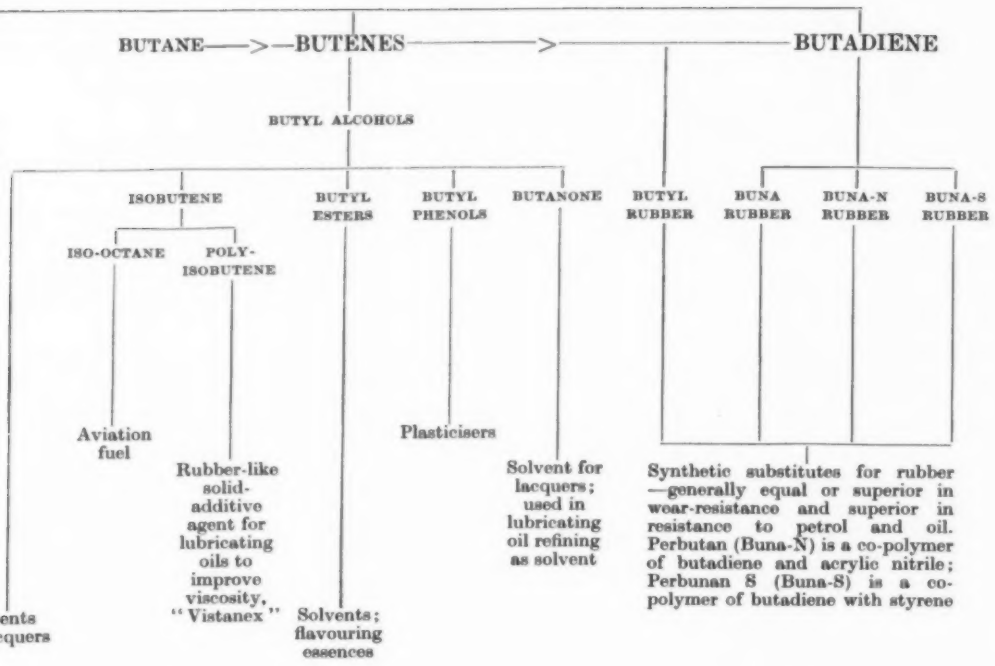
SYNTHETIC PRODUCTS FROM THE CRACKING OF PET



G OF PETROLEUM


LIQUID PRODUCTS
PROPANE —> PROPYLENE
ETHYL ALCOHOL
CHLOROFORM
ACET-ALDEHYDE
ACETIC ACID
ACETONE
ISOPROPYL ALCOHOL
ISOPROPYL ETHER
ISOPROPYL ESTERS
ALLYL CHLORIDE
GLYCERIN
ETHYL BENZENE
STYRENE
PARALDEHYDE
METALDEHYDE
ACETIC ANHYDRIDE
CELLULOSE ACETATE
ETHYL ACETATE
METHACRYLIC ACID AND ESTERS
NITRO-GLYCERIN
TRIACETIN
Anæsthetic
Insecticide; "meta" solid fuel
"Non-flam" film; Basis of most forms of artificial silk textiles. "Acetate Rayon," cement for Triplex non-shatter glass. Transparent sheeting of many kinds and uses
Solvent extensively used for lacquer and varnishes
Solvent, preservative, antiseptic; largely used as alternative to ethyl alcohol
Solvents for lacquers and varnishes
Plasticiser for lacquers
Dyestuff intermediate; medicinal
Solvent used extensively for cordite type explosives and for lub. oil refining
Solvent; anti-knock fuel
Dynamite and blasting powders
Mild acid with extensive uses in many industries such as dyeing, tanning, rubber, rayon textiles, bleaching. Basis of all "acetate" solvents
"Lucite" transparent plastics for mouldings, aeroplane windows ("Perspex") safety glass, optical instruments. Adhesive and textile impregnant
Pharmaceuticals; soaps; toilet preparations; cellophane


LIQUID PRODUCTS
PROPANE
PROPYLENE
ISOPROPYL ALCOHOL
ALLYL CHLORIDE
ACETIC ACID
ACETONE
ISOPROPYL ETHER
ISOPROPYL ESTERS
GLYCERIN
ETHYL ACETATE
METHACRYLIC ACID AND ESTERS
NITRO-GLYCERIN
TRIACETIN
GLYCERYL PHTHALATE "GLYPTAL RESIN"
ACETIC ANHYDRIDE
CELLULOSE ACETATE
Solvent extensively used for lacquer and varnishes
Solvent used extensively for cordite type explosives and for lub. oil refining
Solvent, preservative, antiseptic; largely used as alternative to ethyl alcohol
Solvent; anti-knock fuel
Solvents for lacquers and varnishes
Dynamite and blasting powders
Plasticiser for lacquers
Basis for many varnishes and lacquers and transparent mouldings
Pharmaceuticals; soaps; toilet preparations; cellophane
Solvents for lacquers
" Non-flam " film; Basis of most forms of artificial silk textiles. " Acetate Rayon," cement for Triplex non-shatter glass. Transparent sheeting of many kinds and uses
Mild acid with extensive uses in many industries such as dyeing, tanning, rubber, rayon textiles, bleaching. Basis of all " acetate " solvents
" Lucite " transparent plastics for mouldings, aeroplane windows (" Perspex ") safety glass, optical instruments. Adhesive and textile impregnant


BUTANE
BUTENES
BUTADIENE
BUTYL ALCOHOLS
ISOBUTENE
BUTYL ESTERS
BUTYL PHENOLS
BUTANONE
BUTYL RUBBER
BUNA RUBBER
BUNA-N RUBBER
BUNA-S RUBBER
ISO-OCTANE
POLY-ISOBUTENE
Aviation fuel
Rubber-like solid-additive agent for lubricating oils to improve viscosity, "Vistanex"
Solvents; flavouring essences
Plasticisers
Solvent for lacquers; used in lubricating oil refining as solvent
Synthetic substitutes for rubber —generally equal or superior in wear-resistance and superior in resistance to petrol and oil. Perbutan (Buna-N) is a co-polymer of butadiene and acrylic nitrile; Perbunan 8 (Buna-S) is a co-polymer of butadiene with styrene

[*To face p.* 185.

TABLE XI.

n-Heptane	Octane rating	0
Methylcyclohexane		71
Toluene		104

Furthermore, it should be remembered that toluene has its own particular value as the starting out material for T.N.T. In fact, the "reforming" process is being widely used to-day to bring about the synthesis of such aromatic hydrocarbons which can be segregated from, for example, accompanying paraffins by their superior solubility in specific solvents or by simple azeotropic distillation. From selected cracking stock so high a percentage as 25 of aromatics can be obtained.

The schematic representation in the diagram facing p. 185 shows the present position of synthetics from cracked gases and from the dehydrogenated paraffins. It may confidently be anticipated that this somewhat sparse list of products will be immensely increased in the near future.

Synthetic Products of High Molecular Weight derived from Petroleum.

Some attention must now be given to the production of rubber and plastics, as the latest syntheses from hydrocarbon sources.

In the U.S.A. very extensive plans are being made to replace the serious losses experienced by the United Nations in rubber imports from the Far East. This rubber shortage is extremely acute, and likely to continue so for the duration of the war and for a considerable time after. Clearly the only solution is collaboration between the major rubber users (mainly automobile tyre manufacturers) and the producers of raw materials. At first sight petroleum should be the natural source for butadiene, but considerable stress is being laid on the importance of ethyl alcohol as the primary raw material. The American targets for the production of synthetic rubber are sufficiently impressive. According to Egloff such vast amounts as a million tons a year of various substitutes are contemplated.

Synthetic Rubbers.

The Buna group of substitutes are condensation products of butadiene with acetonitrile or styrene as co-polymerization agents. Tables XII and

TABLE XII.

Butyl Rubber from Cracked Gas.

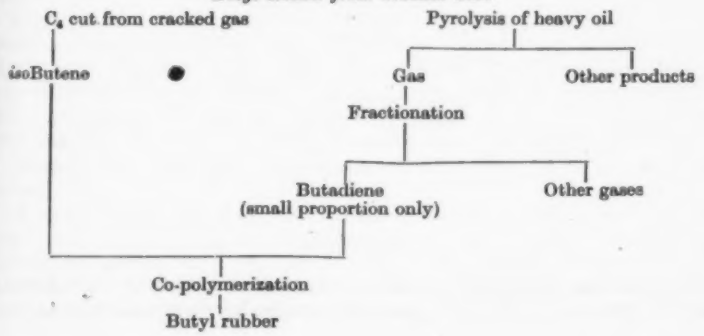
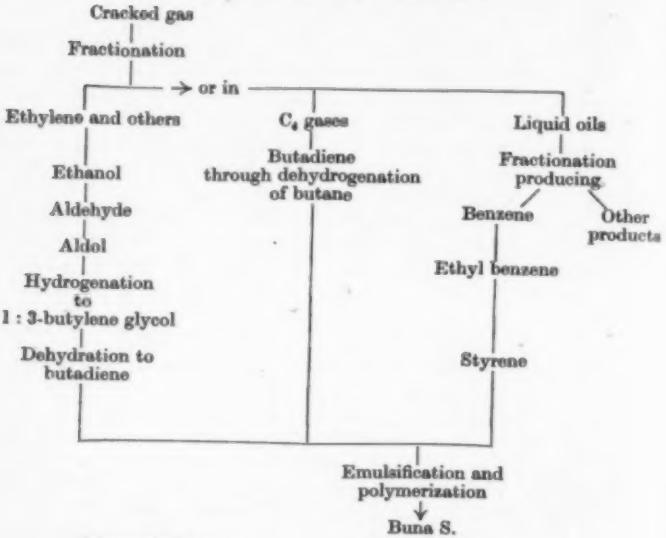
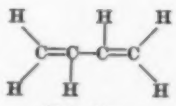


TABLE XIII.

Buna Rubber from Cracked Gas.

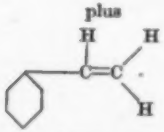


Schematically :—



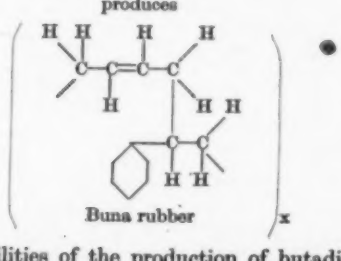
Butadiene

plus



Styrene

produces

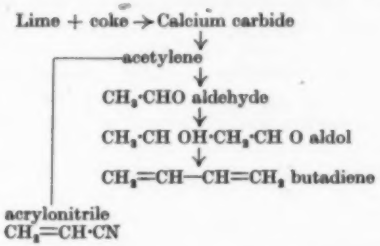


Buna rubber

XIII show the possibilities of the production of butadiene from butane and the butenes. Although apparently simple dehydrogenation is all that

is needed, in fact, the removal of hydrogen under the influence of catalysts is by no means easy, and the alternative route through alcohol (either produced from fermentation processes or from ethylene) to aldehyde, aldol, and final dehydration offers good prospects of success.

Styrene is derived from ethyl benzene, and this, of course, may be regarded as a petroleum derivative. The dehydrogenation of ethyl benzene proceeds at elevated temperature (*circa* 700° C.) in the presence of catalysts. Alternatively, the removal of hydrogen chloride from the chloro-derivative of ethyl benzene yields almost pure styrene. Acrylonitrile again may be synthesized from acetylene—either a coal-lime (carbide) product or a resultant of the high temperature pyrolysis of methane.



Further, acetylene polymerized to vinyl acetylene and added to hydrogen chloride yields chlorobutadiene, which is spontaneously polymerizable to Neoprene. The Thiokols are cross-linked ethylene halides with the sulphur yielded by sodium polysulphide.

Usually the mixture of butadiene and the co-monomer—*e.g.*, acrylonitrile or styrene or methylmethacrylate—is emulsified with water and a wetting agent. Polymerization catalysts, such as peroxides, perborates, or persulphates are added. Modifying agents that control the degree of polymerization and the length of the chain of the linear polymer are employed; such bodies as mercaptans, carbon tetrachloride, or xanthogen disulphide may be used. After several hours and at a temperature *circa* 50° C. a latex is produced, which may be coagulated and treated much as natural latex would be. Inhibitors such as phenyl β-naphthylamine are used to check undue polymerization.

Closely allied to the synthetic rubbers are the high molecular weight resins—all produced by the polymerization or condensation of small units. Space does not permit more than a cursory glance at some of these intriguing materials that are already having a great influence on our everyday life. Polystyrene is derivable directly from petroleum by the polymerization under a variety of conditions and of catalysts of styrene—the dehydrogenation product of ethyl benzene. Polystyrene is of special value as an insulator.

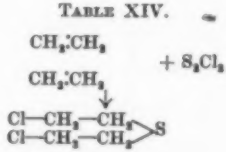
Acetylene from the pyrolysis of methane leads to vinyl alcohol, whose esters yield high-molecular-weight resins. Again, ethylene, *via* ethylene dichloride, yields vinyl chloride, which is the parent material for the synthesis of the polyvinyl chlorides, which can be readily polymerized to form a long straight-chain polymer that may, by selection of co-polymers,

be converted into micro-filaments suitable for weaving. Tubing and hoses also are made of this material and are satisfactory in resisting the action of brine, hydrocarbons, solvents, and acids. From another angle, naphthalene (also a pyrolysis product of petroleum) oxidizes to phthalic acid, which yields complex esters with polyhydric alcohols, *e.g.*, glycerol. Such esters are the basic components for the production of lacquers.

Further, ethylene polymerized under high pressure and in the presence of boron trifluoride yields polythene—a material of superlative insulating properties.

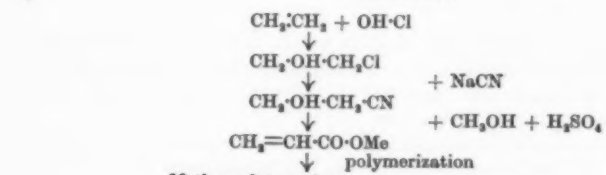
Brief references may be made to Pope's method for the production of mustard gas:

TABLE XIV.



And, further, the well-known acrylic resins:

TABLE XV.



Methacrylate resins.

The Chemist in the Refinery.

Attention has obviously been directed to the vastly important part played by the chemist in the oil-fields. From what has gone before it will be obvious that in the modern refinery and research station he plays an even more important part. Certainly most of the operations therein are *quasi*-engineering. The works chemist must be most closely in touch with his engineering colleague and, in fact, must attain engineering knowledge and experience. It is, indeed, very difficult to discriminate between one or the other in terms of works practice. But at the same time, the chemist must be an interpreter, he must be able to foreshadow impending developments and to indicate the conditions under which the most diverse reactions will proceed. As a case in point, dimerization of *iso*butene may be considered. From the point of view of the chemist, all that is needed is the self-addition of two molecules of *iso*butene. In practice a catalyst is needed, and this may suitably be strong sulphuric acid—agitation is necessary—temperature must be controlled within certain limits—corrosion must be countered. The chemist and the engineer form a potent combination in laying down plant and procedure. And so in every operation in the refinery this collaboration must go on,

and the chemist must always co-operate to the fullest extent with the engineer, even if, as may happen, there arises that most effective entity, the chemical engineer. This entity is not only concerned with the successful running of processes, but must be able to put into practice new and improved methods, operations, and plant. Clearly, the works chemist must be familiar with refinery operations, and must think in terms of full-scale operations. In turn he must feed the research chemist with suggestions as to future investigations. The research chemist working in the research laboratories is concerned not only with new methods of refining, with the nature of products, patents, and patentable processes, but with the whole range of merchantable materials that may be derived from his own raw material. But there is yet another aspect of his work. He must be widely read and closely in touch with the latest chemical and physical investigations. He must always watch out for fresh developments, new syntheses and new compounds, and keep his industrial colleagues fed with recent information. More particularly these days must he realize that the future both of himself and of the industry depends on the up-building of these simple structures—the olefinic gases, and even the radicals derived from the simple paraffins—into worth-while products.

He must learn to build from his chemical bricks not only relatively simple structures like *iso*-octane, but bodies extending to a molecular weight of over 100,000. He must move from elementary molecules into the domains of the colloidal state. In effect, the research chemist in the organization of the petroleum industry must be a leader of thought.

The impact of war not only brings about new needs, but a greater urgency in satisfying these needs. All that has gone before in the development of new and better ways of meeting the requirements of the internal-combustion engine for improved fuel has really been directed to war efforts, especially in the air. Every technical journal in describing this or that improvement in quality has implicitly been regarding their value as a munition of war. Just as everyman's radio was a legacy of the last world war, so will higher efficiency in the aero engine be one result of this. And in fact almost every need of civilized life may and will be met by material derived from mineral oil.

The synthetic developments of the petroleum industry foreshadowed in this lecture have been brought about by the far-seeing efforts of the pioneers responsible for its progress. It would not be out of place to mention here names like Redwood, Edeleanu, Engler, Holde, Midgley, Boyd, Kettering, Brooks, Williams, Grosse, Weiss, Ipatieff, Egloff, Oberfell, and Ellis. All these men have earned an honourable place in the hierarchy of petroleum science—to all of them is due the grateful appreciation of long-lasting work well done.

STANDARD TEMPERATURE FOR SPECIFIC GRAVITY DETERMINATION AND VOLUME CORRECTION.

The following note has been prepared by Sub-Committee No. 1 of the Standardization Committee under the Chairmanship of Mr. H. Hyams, and has been approved by the Standardization Committee and by the Council of the Institute. It is being published in the *Journal* to express the view of the Institute of Petroleum that 60° F. is the standard temperature to which the volume of petroleum products should be corrected when necessary, rather than 20° C. adopted in some other industries.

THE function of I.S.A. 28 (Technical Committee 28 of the International Federation of National Standardising Bodies) is to promote uniformity in methods of testing petroleum throughout the world. One of its sub-committees, I.S.A. 28a-2, is responsible for Density and Specific Gravity. In the early part of 1939 that sub-committee prepared the second draft of a method for the determination of specific gravity of liquid petroleum products, in which specific gravity was defined as the ratio of the weight *in vacuo* of a given volume of the substance at 20° C. to the weight *in vacuo* of an equal volume of water at a temperature of 4° C. It is clear that the intention of the method was to have specific gravities of products reported in terms of densities—grammes per ml. at 20° C. The reason given for the proposal to use 20° C. as the standard or reporting temperature was because this temperature had been generally adopted as the standard or reference temperature in chemical and scientific literature.

When the draft specification was brought to the attention of the A.P.I., the latter felt that the matter was of considerable importance because, if 20° C. were adopted as the temperature for reporting specific gravities, it might also become widely used as the standard temperature to which oil volumes should be adjusted or corrected. It is, of course, known that 60° F. is the temperature which is used exclusively in the oil industry in the United States both for reporting gravities and volumetric quantities.

Discussions on specific-gravity determination and on measurement of oil by volume and by weight have been reported in this journal and in the *Proceedings of the First World Petroleum Congress* held in 1933. The views of the Institute of Petroleum on the reference temperature for specific gravity determinations and the standard temperature to which volume of bulk oil should be corrected are perfectly clear. The brief notes below indicate that on these questions the A.P.I. and the I.P. are in step.

1. *Density and Specific Gravity.*

The standard method for specific gravity determination laid down in the 1935 edition of I.P. "Standard Methods for Testing Petroleum and its Products" stipulated that results should be expressed in terms of sp. gr. 60° F./60° F. signifying that the specific gravity in question is "the ratio of the mass of any given volume of the substance to the mass of a quantity of water which, at 60° F., occupies a volume equal to that of the substance at 60° F." The method also specified that "60° F. shall be employed in petroleum technology as the standard temperature for specific gravity

determinations." The revised 1942 I.P. Specific Gravity Method retains specific gravity 60° F./60° F. at 60° F.; it says, " In general, the standard temperature employed in the oil industry is 60° F. and the results are normally expressed thus, sp. gr. 60° F./60° F."

The B.S.I. has indicated its preference for density in terms of grammes per millilitre at 20° C. and has produced a specification, No. 718–1936, covering Density Hydrometers for this purpose. This method and these instruments are not applicable to the petroleum industry either in the United States or the British Empire.

2. Standard Temperature for Volume Computations.

There have been discussions at meetings of the World Petroleum Congress and of the Institute of Petroleum on measurement of oil by volume and by weight, when the question of standard units and temperatures was ventilated. The view of the Institute is that the Imperial gallon should be retained as the unit of volume in British territories, and that we should remain in line with our American friends by specifying 60° F. as the standard temperature to which oil volumes should, when necessary, be corrected.

I.P. Standardization Sub-Committee 1 is responsible for standardizing matters connected with measurement of petroleum products. That that Committee is keeping to these principles of (1) specific gravity 60° F./60° F. at 60° F. and (2) volume measurements at 60° F. is demonstrated by the following recent or contemplated actions :—

(*a*) In the paper on " Expansion of Crude Petroleum, Petroleum Products and Allied Substances " appearing in the Committee's name in the October 1941 issue of this *Journal*, the specific gravities of products have all been reduced to the common basis sp. gr. 60° F./60° F.

(*b*) The Committee proposes to reconstruct Table 4 of U.S. Bureau of Standards Circular C. 410, *National Standard Petroleum Tables*, replacing the U.S. gallon by the Imperial gallon as the unit of volume. The I.P. table will, however, still be entered against specific gravity 60° F./60° F. at 60° F.

(*c*) Table 2 of U.S. Bureau of Standards Circular C. 410 is to be recast by the Committee so as to facilitate its entry directly against specific gravity 60° F./60° F. at 60° F. instead of A.P.I. gravity at 60° F. Table 2 of the American Circular sets out the volume at 60° F. occupied by unit volume at indicated temperature. The standard temperature of 60° F. will be retained in the reconstructed I.P. table.